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THE PHENOMENA OF MOLECULAR ORIENTATION IN POLAR LIQUIDS AND THEIR SOLUTIONS. PART II. FURTHER DEVELOPMENT OF THE THEORY OF DIPOLE COUPLING IN POLAR LIQUIDS

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This theory assumes the existence of three kinds of coupling to which molecular dipoles are subjected in a solution. The coupling of the first kind (Fowler—Debye) consists in the action of many molecules surrounding the given one and behaving in the solution like a stiffened "cluster". The coupling of the second kind tends to bind the given molecule to its nearest neighbour. Depending on the structure of the molecules, this coupling can give rise to nearly antiparallel or nearly-parallel non-rigid pairs. It plays a predominant part in polar liquids. The coupling of the third kind tends to group quasi-rigid pairs which already exist into double pairs. This kind of coupling does not play any part in dilute solutions (contrary to the coupling of the second kind; cf. Figs 12 and 18). The formation of double pairs is more likely in highly concentrated solutions, and therefore groups of this type play a more important part in concentrated solutions.

It is assumed that for nitrobenzene the coupling of the second kind is nearly antiparallel, while such coupled pairs are able in their turn to align themselves nearly parallel to each other.

On this basis the theory of the four phenomena of molecular orientation: dielectric polarization, the Kerr effect, electric saturation and the Cotton-Mouton effect, was developed. Formulae for the reducing factors of molar constants of these phenomena have been deduced. These are formulae (32), (33), (34) and (45) for the case of nearly antiparallel coupling and (32a), (33a), (34a) and (45) for the case of nearly parallel coupling.

The functions L , P , \mathcal{K} , etc. are defined by formulae (31) and the operations connected with them are determined by formulae (30). The quantities y_1 and y_2 (event. y_3) are the mean coupling energies measured in kT . The variation of the reducing factors for different values of y_1 and y_2 is shown by the curves in Figs. 4, 6, 8 and 10 for nearly antiparallel coupling and in Figs 5, 7, 9 and 10 for nearly parallel coupling. The dependence of y_2 and y_3 on the concentration n of the polar solute in a non-polar solvent (n = the number of dissolved molecules per c. c. of solution) is expressed by formulae (55) and (70) and represented graphically in Figs 12 and 18.

Four constants are needed to define all kinds of molecular coupling in solution. These are the following, and for nitrobenzene they have the values shown in brackets: (1) The energy of coupling of the first kind (always measured in kT)

to which each dipole is subjected ($y'_1=2$); (2) The energy of coupling of the first kind to which the "quasi-rigid" pairs of dipoles as a whole are subjected ($y''_1=1$); (3) The minimum distance at which the molecular dipoles of nitrobenzene approach one another ($r_0=4.6 \text{ \AA}$); this is the only constant (besides the dipole moment μ) necessary for the calculation of the coupling energy of the second kind; (4) The constant ($C=3.5 \times 10^{-108}$) necessary for the calculation of the coupling energy of the third kind as a function of n . — With the help of these constants the reducing factors have been calculated for all four phenomena of molecular orientation, namely: the electric polarization (reducing factor R), the electro-optical Kerr effect (reducing factor R_K), the electric saturation effect (reducing factor R_s) and the Cotton-Mouton effect (reducing factors R_{CM}). These reducing factors are represented graphically in Fig. 20. The curves are very similar to the experimental curves in Fig. 2., calculated with the assumption of an Onsager field.

Of special interest are: the increase of the reducing factor R_{CM} with the concentration; the decrease and afterwards the increase of the reducing factor R of electric polarization (of which a calculation using Lorentz field gives no indication) and finally the very queer course of the reducing factor of the electric saturation R_s very close to the experimental curve. Very significant is the fact, that only by the use of Onsager's idea of the local field is it possible to obtain quantitative agreement between theory and experiment for all four curves of the reducing factors.

§ 1. Introduction. In this paper a further development is presented of the theory published in August 1939 concerning electric polarization, the electro-optical Kerr effect and electric saturation (Piekara 1939 b). Therefore the present paper may be regarded as a sequel not only to Part I of this paper (Piekara 1950), but also to the paper of 1939 mentioned above. For mathematical methods the reader is referred to that work.

Four phenomena of molecular orientation are treated here:

(1) *Electric polarization.* In this effect the molecular polarization $P^{\text{dip}}_{\text{gas}}$ may be expressed by the well-known formula

$$P^{\text{dip}}_{\text{gas}} = \frac{4\pi N \mu^2}{9kT} \quad (1)$$

(N — number of molecules per mol, μ — electric dipole moment), valid for the gaseous state. For liquids, where molecules are not free, the molecular polarization becomes smaller (P^{dip}) and a reducing factor appears:

$$P^{\text{dip}} = P^{\text{dip}}_{\text{gas}} R. \quad (2)$$

(2) *Electric birefringence (Kerr effect).* Gases or liquids, when placed in an external electric field, become birefringent. From measurements of the ellipticity of the light passed through the medium, the molar Kerr constant K^m may be computed according to a well-known expression, which we need not quote here. On the other hand,

the theory of molecular orientations, leads, for gases and vapours, to the formula

$${}_{\text{gas}}K^m = 2\pi N\Theta_2, \quad (3)$$

with

$$\Theta_2 = \frac{2}{45k^2T^2} \mu^2(b_3 - b_1), \quad (4)$$

if the molecules have rotational symmetry ($b_1 = b_2, b_3$) and μ is directed along the axis of symmetry (z — axis). The molar Kerr constant is smaller for the liquid than for the gaseous state and this diminution is taken into account by introducing a reducing factor R_K :

$$K^m = {}_{\text{gas}}K^m R_K. \quad (5)$$

(3) *Electric saturation*. Under the influence of an external electric field E the dielectric constant ε of a gas or a vapour diminishes by

$$\Delta\varepsilon = -12\pi n \left(\frac{\varepsilon + 2}{3} \right)^4 \Theta_3 E^2, \quad (6)$$

if the Lorentz local field is supposed to exist. Here n denotes the number of molecules per c. c. and Θ_3 is the well known Debye expression

$$\Theta_3 = \frac{\mu^4}{45k^2T^3}. \quad (7)$$

Now, we introduce a „molar constant of electric saturation“ in the following way:

$$\text{for gases} \quad {}_{\text{gas}}S^m = -4\pi N\Theta_3, \quad (8)$$

$$\text{for liquids} \quad S^m = -4\pi N\Theta_3 \cdot R_a, \quad (9)$$

where R_a is a reducing factor. According to experiments performed with non-associated liquids, like ethyl-ether, $\Delta\varepsilon$ is negative and R_s nearly 1. On the other hand, experiments carried out by the author and B. Piekara (1936) show that for pure nitrobenzene $\Delta\varepsilon$ is positive, i. e. R_s is negative. This is the so-called „inverse saturation effect“.

(4) *Magnetic birefringence (Cotton-Mouton effect)*. This effect, which takes place in the magnetic field, is analogous to the Kerr effect. In the theory of molecular orientation the molar Cotton-Mouton constant, computed from measurements, is expressed by

$${}_{\text{gas}}C^m = 2\pi N\Theta_1, \quad (10)$$

where

$$\Theta_1 = \frac{2}{45kT} (c_3 - c_1)(b_3 - b_1) \quad (11)$$

($c_1=c_2$ and c_3 are coefficients of magnetic polarizability of the molecule assumed to have rotational symmetry). This constant changes when passing to a liquid state, e. g. it diminishes for many liquids, but increases for nitrobenzene (H. König 1938). We introduce a reducing factor R_{CM} as usual:

$$C^m =_{\text{gas}} C^m R_{CM}. \quad (12)$$

For nitrobenzene we must allow for the fact, that the „reducing“ factor becomes >1 .

We must emphasize that as yet nitrobenzene is the only liquid for which all the effects of molecular orientation here described have been thoroughly investigated. Therefore the experimental results obtained for nitrobenzene can be compared with the theory.

The aim of the theory of intermolecular coupling developed here is to introduce interactions between dipole molecules which could explain the behaviour of reducing factors for all effects of molecular orientation at once. Not only pure nitrobenzene but also its solutions in non-polar solvents will be considered.

§ 2. Experimental values of the reducing factors.

In the first section we have defined four molar constants, namely: P^{dip} , K^m , S^m and C^m . These constants must be computed from experimental data. Nevertheless, experiment does not yield these values immediately but it gives others such as ε , $\Delta\varepsilon$, the phase difference of elliptically polarized light etc., from which the molar constants must be calculated. At first an exact idea about the local field is required for this calculation. Usually Lorentz's local field was applied to gases and vapours as well as to solutions and pure liquids. In such conditions the well known formulae (13)–(16) have been deduced, giving P^{dip} , K^m and S^m . In evaluating C^m we are of course not concerned with the problem of the local field.

The formulae mentioned above are

$$P^{\text{dip}} = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d}, \quad (13)$$

$$K^m = \frac{(n_E - n_X) 6n}{(n^2 + 2)^2 E^2} \left(\frac{3}{\varepsilon + 2} \right)^2 \frac{M}{d}, \quad (14)$$

$$S^m = \frac{\Delta\varepsilon}{3E^2} \left(\frac{3}{\varepsilon + 2} \right)^4 \frac{M}{d}, \quad (15)$$

$$C^m = \frac{(n_H - n_X) 6n}{(n^2 + 2)^2 H^2} \frac{M}{d}. \quad (16)$$

All these molar constants satisfy the rule of additivity. Denoting by X^m any molar constant, we have for the solution

$$X_{12}^m = X_1^m f_1 + X_2^m f_2, \quad (17)$$

where f_1 and f_2 are the molar fractions of the solvent and the solute, and X_{12}^m — the molar constant of the solution, calculated according to (13)–(16) with

$$M_{12} = M_1 f_1 + M_2 f_2. \quad (17a)$$

In the case of the solution of a polar solute (index 2) in a non-polar solvent (index 1), X_1^m and X_{12}^m are to be measured and X_2^m is to be calculated. The latter represents the molar constant of the investigated polar substance at the given concentration. If X^m is measured both for the gaseous ($_{\text{gas}}X^m$) and the liquid state (X_2^m) the reducing factor is obtained immediately form

$$R = \frac{X_2^m}{_{\text{gas}}X^m} \quad (18)$$

On the other hand, if Onsager's local field is assumed, we obtain for the molar constants P^{dip} , K^m and S^m formulae which are essentially different from expression (13)–(15); only formula (16) expressing the molar Cotton-Mouton constant remains unchanged. The peculiar property of these formulae is that the rule of additivity (17) is not applicable. These expressions (in case of Onsager's local field) have been deduced by the author in part I of this paper (Piekara 1950). Here we restrict ourselves to the results:

(a) The molar polarization P_2^{dip} of a polar liquid dissolved in a non-polar solvent is given by the equation

$$\frac{\epsilon_{12}-1}{3g_{12}} \frac{M_{12}}{d_{12}} = P_1 \frac{f_1}{1-r_{12}p_1} + \left[P_2^n + P_2^{\text{dip}} \frac{1}{(1-r_{12}p_2)^2} \right] \frac{f_2}{1-r_{12}p_2}, \quad (19)$$

where

$$g_{12} = \frac{3\epsilon_{12}}{2\epsilon_{12} + 1} \quad (19a)$$

(cavity field factor),

$$r_{12} = \frac{2(\epsilon_{12}-1)}{2\epsilon_{12} + 1} \quad (19b)$$

(reaction field factor), and

$$p_1 = P_1 \frac{d_1}{M_1}, \quad (19c)$$

$$p_2 = P_2^n \frac{d_2}{M_2} \quad (19d)$$

(dielectric polarizability factors of the molecules).

By taking $g_{12} = \frac{\varepsilon_{12} + 2}{3}$ and $r_{12} = 0$ (i. e. $F = \frac{\varepsilon_{12} + 2}{3} E$ and the reaction field vanishes) the case of the Lorentz local field is obtained, and equation (19) is transformed according to the rule of additivity into

$$P_{12} = P_1 f_1 + P_2 f_2 \quad (19e)$$

with

$$P_{12} = \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \frac{M_{12}}{d_{12}} \quad (13a)$$

and

$$P_2 = P_2^n + P_2^{\text{dip}}.$$

(b) The molar Kerr constant K_2^m is to be calculated from the equation

$$K_{12}^m = K_1^m \frac{f_1}{(1 - r_{12} p_1)^2} + K_2^m \frac{f_2}{(1 - r_{12} p_2 \lambda_1)^2 (1 - r_{12} p_2 \lambda_3)^2}, \quad (20)$$

where

$$K_{12}^m = \frac{(n_{12E} - n_{12X}) 6 n_{12}}{(n_{12}^2 + 2)^2 E^2} \frac{1}{g_{12}^2} \frac{M_{12}}{d_{12}}, \quad (20a)$$

and

$$K_1^m = \frac{(n_{1E} - n_{1X}) 6 n_1}{(n_1^2 + 2)^2 E^2} \left(\frac{3}{\varepsilon_1 + 2} \right)^2 \frac{M_1}{d_1}; \quad (20b)$$

$$\lambda_1 = \frac{a_1}{a} \quad \text{and} \quad \lambda_3 = \frac{a_3}{a} \quad (20c)$$

with $a = \frac{1}{3}(a_1 + a_2 + a_3)$ representing a measure of the anisotropy of the molecule assumed to be rotationally symmetric ($a_1 = a_2, a_3$).

Introducing the Lorentz value for g_{12} and taking $r_{12} = 0$ we find that K_{12}^m has a form identical to that of (14) and that the rule of additivity (17) is satisfied:

$$K_{12}^m = K_1^m f_1 + K_2^m f_2. \quad (20d)$$

(c) The molar constant of electric saturation S^m for polar molecules dissolved in a non-polar solvent is to be calculated from the change $\Delta\epsilon_{12}$ of the dielectric constant of the solution under the influence of a strong electric field E . Assuming (as is indeed the case) that $\Delta\epsilon$ for a pure solvent is negligible, the following equation is obtained

$$\frac{\Delta\epsilon_{12}}{3g_{12}^3 E^2} \frac{M_{12}}{d_{12}} = \frac{S_2^m f_2}{\left(1 - \frac{\partial f}{\partial \epsilon}\right) (1 - r_{12} p_2 \lambda_1)^3 (1 - r_{12} p_2 \lambda_3)^4}, \quad (21)$$

where only for Onsager's case and for $a \ll \frac{\mu^2}{kT}$ we get approximately

$$\frac{\partial f}{\partial \epsilon} = \frac{\epsilon_{12} - 1}{2\epsilon_{12} + 1} \left[\frac{1}{\epsilon_{12}} + \left(\frac{\lambda_1}{1 - r_{12} p_2 \lambda_1} + \frac{2\lambda_3}{1 - r_{12} p_2 \lambda_3} \right) \frac{6p_2}{2\epsilon_{12} + 1} \right]. \quad (21a)$$

Putting $g_{12} = \frac{\epsilon_{12} + 2}{3}$ and $r_{12} = 0$ into formula (21), we obtain the Lorentz case, i. e. the additivity of the molar constant S^m , expressed by (15):

$$\frac{\Delta\epsilon_{12}}{3E^2} \left(\frac{3}{\epsilon_{12} + 2} \right)^4 \frac{M_{12}}{d_{12}} = S_2^m f_2,$$

(cf. Part I, § 5).

(d) The molar Cotton-Mouton constant C_2^m may be computed conforming to the rule of additivity:

$$C_{12}^m = C_1^m f_1 + C_2^m f_2, \quad (22)$$

where

$$C_{12}^m = \frac{(n_{12H} - n_{12X}) 6n_{12}}{(n_{12}^2 + 2)^2 H^2} \frac{M_{12}}{d_{12}} \quad (22a)$$

and

$$C_1^m = \frac{(n_{1H} - n_{1X}) 6n_1}{(n_1^2 + 2)^2 H^2} \frac{M_1}{d_1}, \quad (22b)$$

according to (16). As mentioned above, the problem of the local field does not concern the Cotton-Mouton constant because of the low value of the magnetic susceptibility of diamagnetic liquids.

Now, having four molar constants, we are able to calculate the reducing factors according to (18) for all investigated phenomena of molecular orientation, for the Lorentz as well as for the Onsager field. Thus, for different concentrations of nitrobenzene in benzene we ob-

tain four diagrams in the Lorentz case (fig. 1) and four diagrams in the Onsager case (fig. 2), showing the dependence of reducing factors

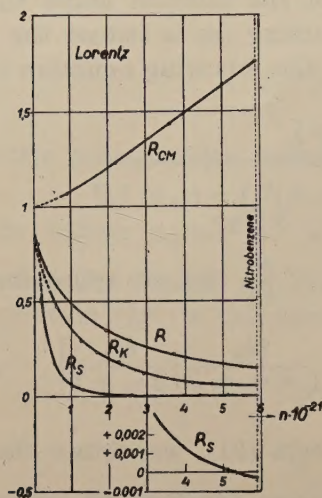


Fig. 1. Curves showing the experimental values of the reducing factors for nitrobenzene in benzene as a function of the number of molecules dissolved per c. c., calculated from experimental data and assuming the existence of a Lorentz local field. The curve R_{CM} is taken from measurements with nitrobenzene — CCl_4 solutions, cf.

Part I, § 6).

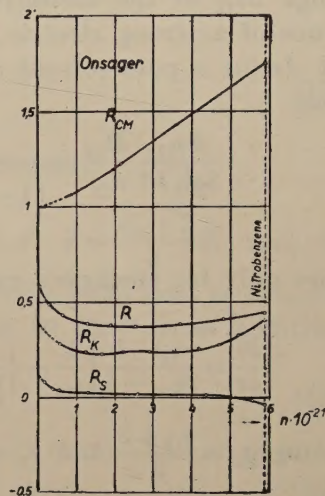


Fig. 2. Curves showing the experimental values of the same reducing factors as in Fig. 1 but calculated assuming the existence of an Onsager local field.

R , R_K , R_S , and R_{CM} on the number n of nitrobenzene molecules per c. c. We call the reducing factors thus obtained „experimental reducing factors“, although they involve a certain theoretical assumption concerning the local field.

§ 3. Discussion of experimental results. If one of the theories of the local field were to lead to the result that all reducing factors for all concentrations are constant and equal to 1, any considerations of intermolecular coupling would be superfluous. Such indeed is the aim of Onsager's theory. For pure polar liquids it does provide formulae which allow us, to calculate the dipole moment, as it would be calculated for a gas, provided we take into account the dielectric polarization.

However, it appears that all the so called „molar constants“ are by no means constants even when Onsager's theory is used, as

shown in fig. 2. In order to explain this variability of the molar constants and of the reducing factors, it appears necessary to assume the presence of intermolecular coupling forces. *It is the purpose of this theory to discover such a mechanism of dipole coupling, which would explain at once the dependence of the reducing factors of all phenomena of molecular orientation on the concentration.*

The question may be put in this way: Which set of graphs, the Lorentz or the Onsager, can be admitted as being nearer to the reality of the observed phenomena? According to Part I of this paper a superiority must be attributed to the Onsager local field¹ and to the corresponding set of reducing factors. Nevertheless, the present theory of molecular coupling will be applied to both sets of reducing factors and it will be shown that the agreement between theory and experiment can be attained only for Onsager's local field.

As to the first set of reducing factors, fig. 1 shows that, with the exception of the reducing factor of the Cotton-Mouton effect, all reducing factors diminish rapidly with concentration. The decrease is especially great in the case of the electric saturation reduction factor R_s , so that the change of sign in the graph of this function (occurring for the number $n = 5,3 \times 10^{21}$ molecules per c. c.) must be shown in a separate diagram with a scale factor 100 times larger. This decrease is due to the Lorentz factor $\left(\frac{\epsilon}{\epsilon+2}\right)^4$ appearing in (15). Such a catastrophic decrease does not occur in the case of Onsager's local field.

In order to explain the diminution of R , R_K and R_s , as well as the change of sign of R_s and the increase of R_{CM} , it was necessary to assume two kinds of dipole coupling forces. On the other hand, if we wish to account for the small increase of R and R_k at high concentrations in the Onsager case, coupling forces of a third kind must be introduced.

§ 4. Three kinds of dipole coupling forces. (a) *Coupling of the first kind.* According to R. H. Fowler (1935) and P. Debye (1935) this coupling is due to a directional field produced by the surrounding molecules ordered as in a crystal lattice. The potential energy of a given molecule is assumed to be

$$U_1 = -W_1 \cos \Theta_1, \quad (23)$$

where Θ_1 is the angular displacement of the dipole axis from the momentary axis of equilibrium A_1 , which can take all possible directions in space.

¹ This is the opinion of many authors (cf. H. Fröhlich, 1946).

(b) *Coupling of the second kind.* This coupling is due to the nearest molecule which at the given moment happens to be in the vicinity of the molecule being considered. We say that two such molecules form a transitory aggregate (a pair). According to the structure of the given molecules, these transitory aggregates can be nearly antiparallel, when the minimum of the potential energy is in the antiparallel orientation of molecules ($\leftarrow\rightarrow$), or nearly parallel, when the molecular dipoles tend to parallel orientation ($\rightarrow\rightarrow$). The first case is assumed for nitrobenzene. It must be emphasized that in this theory the pairs are considered as not rigid; therefore such a pair has no constant resulting moment.

The energy of interaction of two polar molecules is assumed to be of the same form as in the case of the coupling of the first kind:

$$U_2 = -W_2 \cos \Theta_2, \quad (24)$$

Θ_2 being the angular displacement of the dipole axis of the molecule from the momentary axis A_2 of minimum energy. The only difference is that the axes of minimum energy (A_1 in the first and A_2 in the second case) have different properties in both cases. In an external electric field the axis A_1 can take all possible directions in space with equal probability; whereas the axis A_2 , being itself the dipole axis of a molecule, is oriented in space in a quite different manner; owing to this fact, different directions have different probabilities. Mathematically this problem has been treated by the author by an approximate method based on the calculation of the so-called „statistical perturbed averages“ (Piekara 1939 b).

(c) *Coupling of the third kind.* The form of the curves showing the reducing factors of the dielectric polarization and the Kerr effect (fig. 2), especially for higher concentration (an increase of R and R_K), leads to the assumption of the existence of a new kind of coupling, producing aggregates of increased electric moment. In the case of nitrobenzene these aggregates cannot be nearly parallel pairs of simple molecules, because of the particular structure of nitrobenzene which causes nearly antiparallel pairs to manifest their existence by a drop in the curves (fig. 2) for low concentrations. The fact that the increase of R and R_K takes place for higher concentrations indicates that bigger aggregates with increased electric moment are formed. We assume that these aggregates comprise two nearly antiparallel pairs, whose resulting moments μ' are coupled almost parallel. It will be shown that this hypothesis together with the assumption of the first and second kind of coupling is quite sufficient to give an account of the

general behaviour of the reducing factors, especially for high concentrations.

The exact calculation with this kind of coupling presents difficulties impossible to overcome. Nevertheless, the most important peculiarities of the curves result almost exclusively of the two first kinds of coupling. Therefore the coupling of the third kind will be taken into account only in a very approximate manner, that is the transitory pairs of molecules will be considered as rigid with regard to the external electric field and as having an average electric moment μ' . The mutual potential energy of two such pairs is expressed by a formula similar to (24), viz.

$$U_3 = -W_3 \cos \Theta_3. \quad (25)$$

Moreover, the resulting moments of these pairs are subject to the coupling of the first kind, like the single dipole molecules in liquids.

In the following section, formulae for the reducing factors for electric polarization (R), the electro-optical Kerr effect (R_K) and electric saturation (R_s) will be given; they were computed by the author in the paper (1939 b) mentioned above by the assumption of two kinds of coupling. The magnetic birefringence, which has not been taken into account in the above paper, will be treated with more details in Section 6 of this paper.

Further development of this theory, the application of the coupling of the third kind and the comparison with experiment will be the subject of the remaining sections.

§ 5. The reducing factors for electric polarization, electro-optical Kerr effect and electric saturation. In the first part of this work, in Sections 3, 4 and 5 formulae have been computed for the molar constants P_2^{dip} , K_2^m and S_2^m of the above-mentioned phenomena, assuming the local field to be either of the Lorentz or of the Onsager type.

These formulae have been quoted in Section 2 of the present paper as formulae (19), (20) and (21). If the values of the coefficients g and r corresponding to the Lorentz field $\left(\frac{\epsilon_{12}+2}{3} \text{ and } 0\right)$ or to the Onsager field $\left(\frac{3\epsilon_{12}}{2\epsilon_{12}+1} \text{ and } \frac{2(\epsilon_{12}-1)}{2\epsilon_{12}+1}\right)$ are substituted in these equations, the Lorentz-Debye or the Onsager-Debye formulae are obtained.

In the calculation of these formulae in Part I of this work the statistical mean values of $\cos \Theta$ and $\cos^2 \Theta$ have been obtained on the assumption that the molecules are completely free and therefore:

$$\left. \begin{aligned} \overline{\cos \Theta} &= \frac{1}{3}x - \frac{1}{45}x^3 + \dots \\ \overline{\cos^2 \Theta} &= \frac{1}{3} + \frac{2}{45}x^2 + \dots, \end{aligned} \right\} \quad (26)$$

where

$$x = \frac{\mu^* F^*}{kT}.$$

μ^* and F^* are determined by the formulae (54) and (55). It turned out however, that the numerical values of the molar constants (X_2^m) were different from $_{\text{gas}}X^m$ and therefore the „experimental values“ of the reducing factors R , R_K and R_s were calculated by formula (18) (these values are represented graphically by the diagrams in figs 1 and 2). This would correspond to introducing empirical coefficients R , R_K and R_s into (26) as coefficients of x , x^2 and x^3 respectively.

These coefficients have been calculated in the author's former paper (1939 b) on the assumption of the existence of the first two kinds of coupling forces. The so-called „statistical perturbed averages“ must be used instead of the usual statistical means:

$$\overline{M(\cos \Theta)^*} = \frac{1}{3}xR - \frac{1}{45}x^3R_s, \quad (28)$$

$$\overline{M(\cos^2 \Theta)^*} = \frac{1}{3} + \frac{2}{45}x^2R_K. \quad (29)$$

The fact that now $x = \frac{\mu^* F^*}{kT}$ (in the former paper $x = \frac{\mu F}{kT}$) does not influence the results. The reducing factors R , R_K and R_s , fulfilling relation (18), are expressed by formulae (16), (33) and (41) of the above-mentioned paper and so the „theoretical values of the reducing factors“ are obtained. These formulae have a rather cumbersome form; a more suitable form may be obtained as follows.

Denote by $F(Y)$ a function of y_1 and y_2 where y_1 and y_2 are, as previously, the energies of coupling of the first and second kind respectively, expressed in kT -units. Introduce the following symbols

$$\left. \begin{aligned} \widetilde{\widetilde{F}}(\widetilde{\widetilde{Y}}) &= \widetilde{\widetilde{F}} = \frac{1}{6}F(y_1 + y_2) + \frac{1}{6}F(y_2 - y_1) + \frac{2}{3}F(\sqrt{y_1^2 + y_2^2}), \\ \widetilde{\widetilde{F}}(\widetilde{\widetilde{Y}})' &= \widetilde{\widetilde{F}}' = \frac{1}{6}F(y_1 + y_2) + \frac{1}{6}F(y_2 - y_1) + \frac{2}{3} \frac{y_2}{\sqrt{y_1^2 + y_2^2}} F(\sqrt{y_1^2 + y_2^2}), \\ \widetilde{\widetilde{F}}(\widetilde{\widetilde{Y}})'' &= \widetilde{\widetilde{F}}'' = \frac{1}{6}F(y_1 + y_2) + \frac{1}{6}F(y_2 - y_1) + \frac{2}{3} \frac{y_2^2 - \frac{1}{2}y_1^2}{y_1^2 + y_2^2} F(\sqrt{y_1^2 + y_2^2}) \end{aligned} \right\} \quad (30)$$

and make use of the following hyperbolic functions

$$\left. \begin{aligned}
 L(Y) &= L = \operatorname{ctgh} Y - \frac{1}{Y}, \\
 P(Y) &= P = 1 - 3 \frac{L}{Y}, \\
 \mathcal{K}(Y) &= \mathcal{K} = 3 \frac{L}{Y} \left(2 - 3 \frac{L}{Y} - 2L^2 \right), \\
 \mathcal{S}(Y) &= \mathcal{S} = 1 - 3 \frac{L}{Y} - L^2, \\
 \mathcal{s}(Y) &= \mathcal{s} = L \left(1 - 2 \frac{L}{Y} - L^2 \right), \\
 R^*(Y) &= R = 3 \left[1 - 4L^2 + 3L^4 + 4 \frac{L}{Y} (2L^2 - 1) + 6 \frac{L^2}{Y^2} \right], \\
 \mathcal{C}(Y) &= \mathcal{C} = 3 \frac{L}{Y} \left(2 - 3 \frac{L}{Y} \right).
 \end{aligned} \right\} \quad (31)$$

Then the reducing factors R , R_K and R_s can be expressed in a relatively simple form, as follows:

(1) *Electric polarization*, (a) when nearly antiparallel coupling of the second kind is assumed

$$R = \frac{1 - \tilde{L}^2}{1 + \tilde{L}}, \quad (32)$$

(b) on the other hand in the case of nearly parallel coupling odd functions change their signs and we obtain

$$R = \frac{1 - \tilde{L}^2}{1 - \tilde{L}}. \quad (32a)$$

(2) *Electric birefringence*, (a) in the case of nearly antiparallel coupling

$$R_K = \frac{\tilde{\mathcal{K}} - 6R \frac{\tilde{L}^2}{Y}}{1 - \tilde{P}''}. \quad (33)$$

where R is expressed by formula (32),

(b) in the case of nearly parallel coupling

$$R_K = \frac{\tilde{\mathcal{K}} + 6R \frac{\tilde{L}^2}{Y}}{1 - \tilde{P}''}, \quad (33a)$$

where R is to be calculated from formula (32a).

(3) *Electric saturation effect*, (a) in the case of nearly antiparallel coupling

$$R_s = \frac{\widetilde{R}^* - 2R_K \widetilde{S}'' - 9R \widetilde{S}'}{1 + \widetilde{L}'}, \quad (34)$$

(b) in the case on nearly parallel coupling

$$R_s = \frac{\widetilde{R}^* - 2R_K \widetilde{S}'' + 9R \widetilde{S}'}{1 - \widetilde{L}'}, \quad (34a)$$

where R and R_K are to be calculated from the preceding formulae for the proper type of coupling. The calculation of the reducing factors from the formulae given above is rather cumbersome. For the sake of facility all necessary functions have been represented graphically in fig. 3, from which values for the required Y 's ($=y_1 + y_2$, or $y_2 - y_1$,

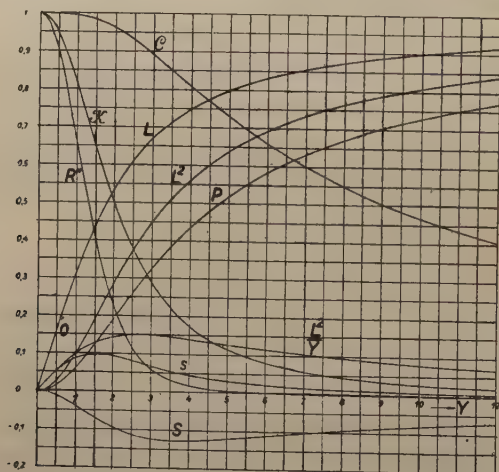


Fig. 3. Graphs of the hyperbolic function used.

or $\sqrt{y_1^2 + y_2^2}$) may be obtained by interpolation. This interpolation has been performed from large graphs drawn on millimetre paper yielding an accuracy to the third decimal figure. On this basis the reducing factors have been calculated according to formulae (32) to (34a). Graphs representing the reducing factors as function of y_2 for different values of y_1 are represented in fig. 4—9².

² In these figures and in Fig. 10 the symbol \neg stands for \neg and in Figs. 6 and 7 \mathcal{K} stands for \mathcal{K} .

Corrigendum to Fig. 3 and 4 of my paper 1939 b: the figures on the axis of abscissae should be multiplied by 10.

An interesting phenomenon can be seen from the curves in fig. 4, viz. the cooperation between the coupling of both kinds, which when acting separately diminish the reducing factor. On the other hand, when both kinds of coupling forces act simultaneously they help each other if they are weak couplings;

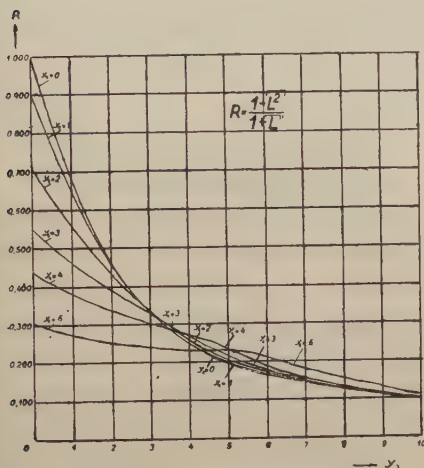


Fig. 4. Dependence of the reducing factors for the electric polarization on y_2 for nearly antiparallel coupling and for different values of y_1 .

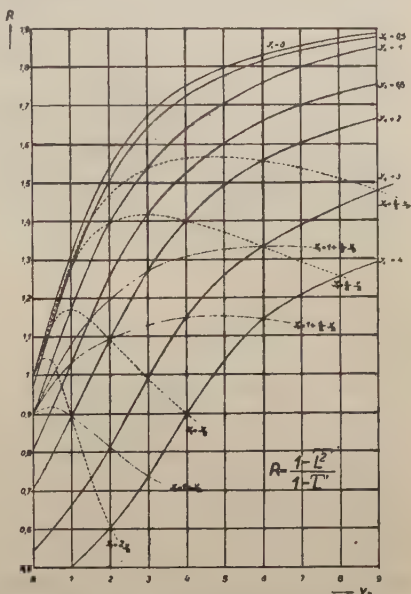


Fig. 5. The same dependence $R(y_2)$ as in Fig. 4 but for nearly parallel coupling.

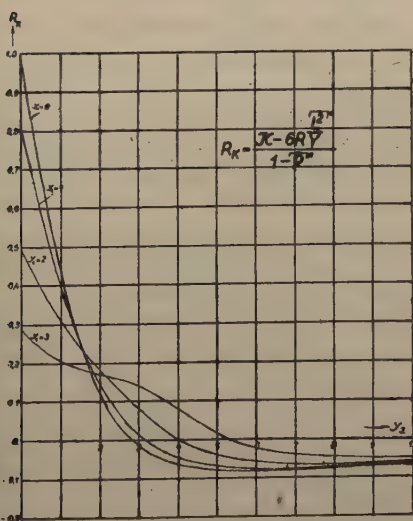


Fig. 6. Reducing factors for the electro-optical Kerr effect as functions of y_2 for different values of y_1 ; nearly antiparallel coupling.

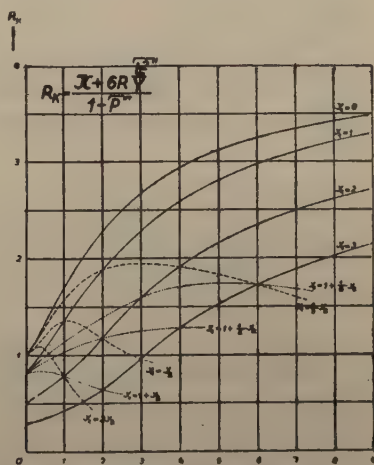


Fig. 7. Reducing factors R_K as in Fig. 6 but for nearly parallel coupling.

stronger couplings begin to disturb one another, causing an increase in the reducing factor. This effect appears to a much higher degree in the graph of the reducing factors R_K and R_s , as shown by the sets of curves in figs 6 and 8. We can conclude that the coupling forces of the first kind tend to separate the molecules linked by coupling forces of the second kind.

In the case of nearly parallel coupling the cooperating coupling of the first kind causes only a considerable diminution of the reducing factors, as shown in the graphs in figs 5, 7 and 9. Besides the curves

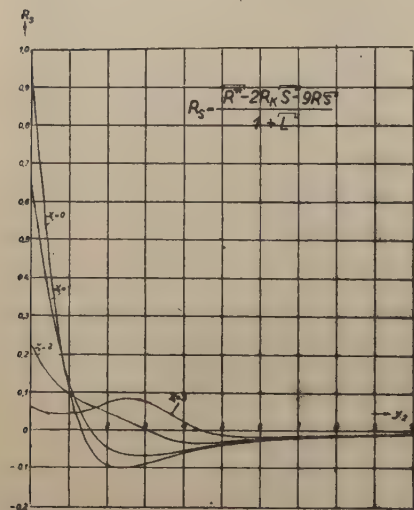


Fig. 8. Curves showing the reducing factors for the electric saturation effect; nearly antiparallel coupling.

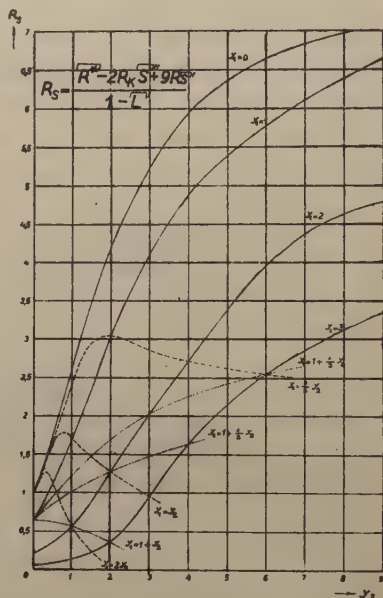


Fig. 9. Curves showing the reducing factors for the electric saturation effect; nearly parallel coupling.

for $y_1=0, 0.5, 1$ etc. there are some curves for varying values of y_1 , viz. for $y_1=ay_2$ (broken lines) and for $y_1=1+ay_2$ (dotted lines).

One more distinctive feature of nearly antiparallel coupling must be noted here, namely, the reducing factors of the electro-optical Kerr effect and electric saturation become negative if the value of y_2 alone has a sufficiently large value. This means that when the coupling of the second kind is sufficiently strong both the Kerr effect and the electric saturation effect change their signs.

The mechanism of these phenomena may be explained as follows. Suppose that the electric moment of the molecule lies in the direction of the axis of highest polarizability. In this case the Kerr effect is

positive, i. e. the Kerr constant $_{\text{gas}}K^m > 0$, as is to be seen from formulae (3) and (4). When a sufficiently strong antiparallel coupling appears, the resulting moment of a molecular pair becomes perpendicular to the axis of highest polarizability and the Kerr effect becomes negative. The possibility of such a change of sign of the Kerr effect was mentioned by Briegleb (1937) in his book. Inasmuch as this phenomenon does not occur in nitrobenzene, it may be assumed that the energy of the coupling of the second kind is not high enough, but it is quite sufficient to produce the „inverse saturation effect“, which has really been observed in the case of nitrobenzene for sufficiently concentrated solutions.

The mechanism of the inverse saturation effect is more complicated, in conformity with the more complicated character of formula (34). This formula contains two negative terms. The first one $-2R_K\hat{S}''$, is negative only for $R_K < 0$, since the function S is always negative. Thus, the first contribution to the inverse saturation effect consists of the negative Kerr effect. In this case both dipole moments of a molecular pair tend to become perpendicular to the external electric field. This circumstance causes an increase of the dielectric constant instead of a diminution as in the normal saturation effect. This contribution, however, cannot take place in nitrobenzene because of the positive Kerr effect.

The second contribution to the inverse saturation effect is connected with the term $-9R\hat{S}'$ which is always negative. In the case of nitrobenzene solution this term can exceed the two preceding positive terms only in the case of a highly concentrated solution. It seems that the mechanism of this contribution to the inverse saturation effect may be represented as a „closing of dipole scissors“. The scissors are formed by two dipoles momentarily linked together in a nearly antiparallel pair. The resulting moment of such a pair, and the moments of the individual dipoles have a tendency to be oriented parallel to the external electric field. Thus, the „scissors“ slightly „closed“ produce, statistically, a small increase in the resulting moment and in consequence a small rise of the dielectric constant of the liquid, i. e. an inverse saturation effect.

Returning to the case of nearly parallel coupling, the reducing factors tend asymptotically to limiting values when $y_1 = 0$ and $y_2 \rightarrow \infty$. These limiting values are: $R=2$, $R_K=4$ and $R_s=8$. This means that an extremely strong coupling creates in the liquid $N/2$ pairs each having a double electric moment; since $y_1=0$ these pairs may be considered

as free. Under such conditions the formulae of section 1 can be applied, yielding the above limiting values. For instance

$$S^m = -4\pi \left(\frac{N}{2} \right) \frac{(2\mu)^4}{45k^3T^3} = -4\pi N \frac{\mu^4}{45k^3T^3} \cdot 8 = 8 \cdot_{\text{gas}} S^m.$$

The first traces of such an increase of the dielectric saturation effect would be expected in dilute solutions of alcohols in non-polar solvents. Hitherto such experiments have been lacking, however.

§ 6. Reducing factor for magnetic birefringence. The Cotton-Mouton constant is defined by the formula (92) in Part I of this paper:

$$C^m = \frac{R_H - R_X}{H^2}. \quad (35)$$

The molecular refractivities R_H and R_X are expressed by formulae similar to these for R_E and R_X in the Kerr effect (v. Section 4 of Part I of this paper):

$$R_H = \frac{4\pi}{3} N \overline{M(\gamma_H)}^* \quad \text{and} \quad R_X = \frac{4\pi}{3} N \overline{M(\gamma_X)}^*, \quad (36)$$

where

$$\left. \begin{aligned} \overline{M(\gamma_H)}^* &= b_1 + (b_3 - b_1) \overline{M(\cos^2 \Theta)}^* \\ \text{and} \quad \overline{M(\gamma_X)}^* &= \frac{1}{2}(b_1 + b_3) - \frac{1}{2}(b_3 - b_1) \overline{M(\cos^2 \Theta)}^*. \end{aligned} \right\} \quad (37)$$

Hence

$$C^m = 2\pi N \frac{b_3 - b_1}{H^2} \left[\overline{M(\cos^2 \Theta)}^* - \frac{1}{3} \right]. \quad (38)$$

Thus, the calculation of C^m is reduced to the calculation of the perturbed statistical average $\overline{M(\cos^2 \Theta)}^*$.

This average can be calculated by methods similar to those used in an earlier paper by the author (1939 b). The essential difference is in the expression for the potential energy of the molecule which, when an external magnetic field is applied, has the form

$$U = -W \cos \Theta' - \frac{1}{2}(c_3 - c_1) H^2 \cos^2 \Theta, \quad (39)$$

where c_3 and c_1 are the components of the magnetic polarizability of the molecule in the direction of the axis of symmetry and in the perpendicular direction respectively; other symbols are defined as in the above quoted paper. Denoting for brevity

$$x' = \frac{c_3 - c_1}{2kT} H^2, \quad (40)$$

we have

$$M(\cos^2 \Theta) = \frac{\overline{\cos^2 \Theta \ y \cos \Theta' + x' \cos \Theta}}{e y \cos \Theta' + x' \cos \Theta} = M^0(\cos^2 \Theta) + x' \{ M^0(\cos^4 \Theta) - [M^0(\cos^2 \Theta)]^2 \} + \dots \quad (41)$$

The perturbed statistical average $\overline{M(\cos^2 \Theta)^*}$ may be obtained by first calculating

$$\left. \begin{aligned} \overline{M^0(\cos^2 \Theta)^*} &= \left(1 - 3 \frac{L}{Y}\right)'' \overline{M(\cos^2 \Omega_2)^*} + \frac{1}{3} \left[1 - \left(1 - 3 \frac{L}{Y}\right)''\right], \\ \overline{M^0(\cos^4 \Theta)^*} &= \frac{1}{5}, \\ \overline{[M^0(\cos^2 \Theta)]^2}^* &= \frac{1}{5} \left(1 - \frac{8L}{3Y} + 4 \frac{L^2}{Y^2}\right), \end{aligned} \right\} \quad (42)$$

then inserting these expressions in the formula

$$\overline{M(\cos^2 \Theta)^*} = \overline{M^0(\cos^2 \Theta)^*} + x' \{ \overline{M^0(\cos^4 \Theta)^*} - \overline{[M^0(\cos^2 \Theta)]^2}^* \} \quad (43)$$

and applying the very essential condition, valid both for nearly parallel and nearly antiparallel coupling,

$$\overline{M(\cos^2 \Theta)^*} = \overline{M(\cos^2 \Omega_2)^*},$$

we obtain finally

$$\overline{M(\cos^2 \Theta)^*} = \frac{1}{3} + \frac{4}{45} x' R_{CM}, \quad (44)$$

where

$$R_{CM} = \frac{\overline{\mathcal{C}}}{1 - \overline{P}''}. \quad (45)$$

Introducing formula (44) into (38), gives

$$C^m = 2\pi N \frac{2}{45kT} (b_3 - b_1)(c_3 - c_1) R_{CM} = 2\pi N \Theta_1 R_{CM}.$$

Thus, R_{CM} expressed by (45) is the reducing factor of the magnetic birefringence for both nearly parallel and nearly antiparallel coupling.

Curves showing dependence of R_{CM} on y_2 for different values of y_1 are represented in fig. 10. The increase of R_{CM} for $y_1 = \text{const.}$ and its asymptotic approach towards $R_{CM} = 2$, when $y_1 = 0$ and $y_2 \rightarrow \infty$, will be noted. The sets of curves both for $y_1 = ay_2$ (broken lines) and

for $y_1=1+ay_2$ (dotted lines) show that the coupling of the first kind diminishes the reducing factor of the Cotton-Mouton effect as well

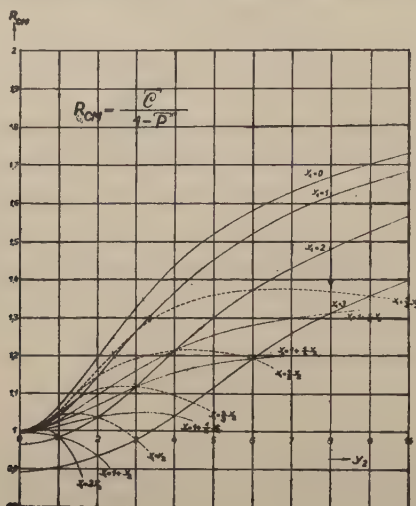


Fig. 10. Reducing factors for the Cotton-Mouton effect for both nearly parallel and nearly antiparallel coupling.

as the reducing factors of all the other phenomena of molecular orientation.

§ 7. Relation between coupling energy and concentration. Reducing factors computed in the foregoing paragraphs depend on y_1 and y_2 , i. e. on the coupling energy of both kinds expressed in kT -units. Coupling of the first kind is present in infinitely diluted as well as in concentrated solutions and pure liquids. Nevertheless y_1 depends on the concentration of the solution, but this dependence is very slight compared to the dependence of y_2 on the concentration of the solution which, as will be seen, is extremely intense. Since in a dilute solution the molecular dipoles are very distant from one another, there is only a slight probability of their coming close together and therefore the mean value of the coupling energy of the second kind (y_2) is small. With increasing concentration the values of y_2 must also grow considerably; the relation $y_2(n)$ then becomes the predominant one. On the other hand, with regard to y_1 , comparison of the theory with experimental results (v. § 9) shows that it is possible to assume a constant value for y_1 for all concentrations of the solution.

The precise computation of y_2 is, strictly speaking, impossible. The value of y_2 depending on the distance between the molecules r should be taken into account by the determination of $\overline{M(\cos^m \Theta)^*}$, a procedure which would extremely complicate the theory and restrict its application. Besides it would not add anything essentially new, for in the phenomena of molecular orientation the deciding factor is the influence of the external field on the angular positions of the molecules, and not on their distances apart³. Therefore in the determination of the statistical perturbed average of the function $\cos^m \Theta$ a certain mean value for y_2 has been used. Now, its relation to the concentration must be approximately determined.

The experimental evidence shows that it is sufficient to assume that the coupling energy W_2 in case of a nitrobenzene molecule pair is of the form μ^2/r^3 . The energy of coupling W_2 , used in this theory, should be understood to be the mean value of the expression μ^2/r^3 determined from all double molecular aggregates actually occurring:

$$W_2 = \mu^2 \overline{r^{-3}}; \quad (46)$$

therefore

$$y_2 = \frac{\mu^2}{kT} \overline{r^{-3}}. \quad (47)$$

Now, the mean statistical value $\overline{r^{-3}}$ must be determined.

Let us imagine that in the solution of a polar liquid of concentration n in a non-polar solvent (n — number of dipole molecules in unit volume of the solution), the molecular dipoles are situated in regularly spaced positions. If every molecule were enveloped by a sphere of a radius ϱ such that it would touch all the neighbouring spheres, then such a collection of spheres of maximum density would fill 74% of the whole space. The radius ϱ can be determined from the equation

$$\frac{4\pi\varrho^3}{3} n = 0,74,$$

hence

$$\varrho = \frac{0,561}{\sqrt{n}}.$$

³ The relation between the energy of coupling and the distance apart, and form of the molecules was taken into account by R. Fuoss (1934) but complicated the theory to such a degree that it was only possible to determine the polarization, and that only subject to narrow restrictions. Besides Fuoss did not take into consideration the coupling with the solvent. On account of these and other causes the comparison of his results with the experiments made by Professor J. Rayski (unpublished), did not turn out favourably.

The distance between neighbouring molecules is therefore

$$R = \frac{1,122}{\sqrt[3]{n}}. \quad (48)$$

If the molecules are now let loose some of them will change places because of their tendency to disorder. It is evident that every molecule has a nearest neighbour at every moment. Such a pair of molecules will be termed simply a „double aggregate“ or a „pair“ assuming that the „pair“ is not regarded as stable and still less as rigid.

Let r be the distance between the two molecules of the pair; and assume that r can vary between a certain minimum value r_0 and a maximum value R . Assume further that the formation of groups consisting of more than two molecules is so rare that it need not be taken into account. This last assumption is particularly justified in the case of nearly antiparallel coupling, since a quadrupole has a field of very short range and does not attract a wandering dipole with as great a force as a single dipole.

Let us consider a certain molecule whose nearest neighbour can move between two concentric spherical surfaces of radii r_0 and R . Let the dipole of one of these neighbouring molecules make an angle Θ_2 with the axis of minimum potential energy passing through the axis of the dipole of the other. Both this angle and the distance r between the molecules change their values continually in space and time. The probability that the distance separating the molecules has a value between r and $r+dr$ and that the angle between the two molecules lies between Θ_2 and $\Theta_2+d\Theta_2$ is then

$$Ae^{-\frac{u}{kT}} 4\pi r^2 dr \cdot 2\pi \sin \Theta_2 d\Theta_2. \quad (49)$$

The coefficient A can be determined from the condition that the probability of forming a couple with a distance separating the molecules between r_0 and R is equal to 1, i. e.

$$1 = 8\pi^2 A \int_{r_0}^R r^2 dr \int_0^\pi e^{-\frac{u}{kT}} \sin \Theta_2 d\Theta_2.$$

Thus, the probability of forming a couple with a distance separating the molecules between r and $r+dr$ is

$$p = \frac{r^2 dr \int_0^\pi e^{-\frac{u}{kT}} \sin \Theta_2 d\Theta_2}{\int_{r_0}^R r^2 dr \int_0^\pi e^{-\frac{u}{kT}} \sin \Theta_2 d\Theta_2} \quad (50)$$

The number of pairs dn' whose constituent dipoles lie between r and $r+dr$ is then

$$dn' = \frac{n}{2} p \quad (51)$$

These formulae allow us to determine the mean value of r^{-3} :

$$\overline{r^{-3}} = \frac{2}{n} \int_{r_0}^R r^{-3} dn' = \frac{\int_{r_0}^R \frac{dr}{r} \int_0^\pi e^{-\frac{u}{kT}} \sin \Theta_2 d\Theta_2}{\int_{r_0}^R r^2 dr \int_0^\pi e^{-\frac{u}{kT}} \sin \Theta_2 d\Theta_2} \quad (52)$$

Consequently from formula (47) the coupling energy y_2 may be determined.

In the case of nitrobenzene we have assumed that the molecules have a tendency towards nearly antiparallel coupling; for this substance the energy of an aggregate of two molecular dipoles is expressed by the formula

$$u = -\frac{\mu^2}{r^3} \cos \Theta_2, \quad (53)$$

provided that the distance r is not very much greater than r_0 . Under this condition, if the shape of the molecule is elongated (as in the case of nitrobenzene), there is a tendency to nearly antiparallel coupling. On the other hand, for greater distances the coupling may differ from the nearly antiparallel type and the energy should be expressed by a more general formula. But then the Boltzman factor $e^{-\frac{u}{kT}}$ has a very small value compared to its value when r approaches r_0 . We may employ for this factor the expression

$$e^{\frac{\mu^2}{kTr^3} \cos \Theta_2}.$$

Although, strictly speaking, this expression applies only in the neighbourhood of the lower limit of integration the error in the value of

the integral in (52) introduced by this simplification will be very small since this value depends chiefly on the magnitude of the integrand in the neighbourhood of $r=r_0$.

Thus, combining formulae (47), (52) and (53), we obtain

$$y_2 = a \frac{\int_{r_0}^R \frac{dr}{r} \int_0^\pi e^{\frac{a}{r^3} \cos \Theta_2} \sin \Theta_2 d\Theta_2}{\int_{r_0}^R r^2 dr \int_0^\pi e^{\frac{a}{r^3} \cos \Theta_2} \sin \Theta_2 d\Theta_2}, \quad (54)$$

where

$$a = \frac{\mu^2}{kT}. \quad (54')$$

The integration with respect to Θ_2 can be accomplished immediately yielding

$$y_2 = a \frac{\int_{r_0}^R r^2 \sinh \frac{a}{r^3} dr}{\int_{r_0}^R r^5 \sinh \frac{a}{r^3} dr}. \quad (55)$$

Both integrals have been calculated graphically. For nitrobenzene ($\mu=4,23 \times 10^{-18}$) at 293°K $a=0,443 \times 10^{-21}$. The only arbitrary con-

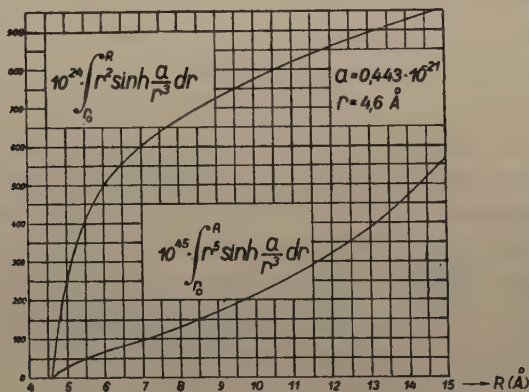


Fig. 11. Graphs of the integrals appearing in formula (55) as a function of the upper limit R .

stant appearing in these integrals is r_0 . To obtain agreement with experiment it was assumed that $r_0=4,6 \text{ \AA}$. Considering the fact that

the diameter of a molecule of benzene is about $4,1 \text{ \AA}$ (Stuart 1934), which means that two benzene rings are able to approach each other to within that distance, and further that in liquid nitrobenzene ($n=5,88 \times 10^{21}$) the average intermolecular distance is $R=1,122/\sqrt[3]{n}=6,22 \text{ \AA}$, then the assumption $r_0=4,6 \text{ \AA}$ seems to be a reasonable one.

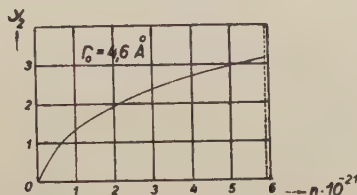


Fig. 12. Variation of the coupling energy of the second kind with the number of molecules per c. c.

Both integrals of expression (55), calculated on the above assumption, are represented graphically in fig. 11. Using them the coupling energy y_2 can be calculated for different concentrations n (see formula (48)). The relation $y_2(n)$ is represented by the curve in fig. 12.

§ 8. Comparison with experimental data. First, we shall compare the results of the theory with experiment in two limiting cases, viz.

(1) On the assumption of the existence of a coupling of the first kind only,

(2) On the assumption of the existence of a coupling of the second kind only.

In the first case ($y_1 \neq 0, y_2 = 0$) the formulae for the reducing factors take the following form

$$R=1-L^2, \text{ (Fowler 1935, Debye 1935 a),} \quad (56)$$

$$R_K=\mathcal{K}(y_1)=3\frac{L}{y_1}\left[2-3\frac{L}{y_1}-2L^2\right] \text{ (Friedrich 1937),} \quad (57)$$

$$R_s=R^*(y_1)=3\left[1-4L^2+3L^4+4\frac{L}{y_1}(2L^2-1)+6\frac{L^2}{y_1^2}\right] \text{ (Debye 1935 b),} \quad (58)$$

$$R_{CM}=C(y_1)=3\frac{L}{y_1}\left(2-3\frac{L}{y_1}\right) \text{ (Piekara 1939 a).} \quad (59)$$

These factors are represented graphically in fig. 13. On comparing them with the experimental values calculated on the basis either of the Lorentz or of the Onsager field (figs 1 and 2) we do not perceive

any resemblance at all. The differences in the characters of the curves are very striking: R_s does not change sign, as the experimental results require, and the curve for R_{CM} falls instead of rising, as is the case with the experimental curve.

In the second limiting case in which coupling of the second kind (nearly antiparallel) alone exists, we have $y_1=0$, $y_2 \neq 0$ and the reducing factors amount to

$$R = 1 - L, \quad (60)$$

$$R_K = 2 - 3 \frac{L}{y_2} - 2L^2, \quad (61)$$

$$R_s = 6 \frac{L}{y_2} - (1 - L)(1 + 5L), \quad (62)$$

$$R_{CM} = 2 - 3 \frac{L}{y_2}. \quad (63)$$

The corresponding curves are represented in fig. 14. We see that the curve for R_{CM} is rather similar to the experimental curve and that R_s

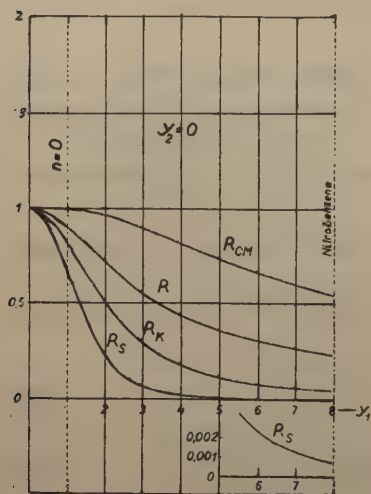


Fig. 13. Dependence of the reducing factors on y_1 , expressed by formulae (56)–(59) when $y_2=0$.

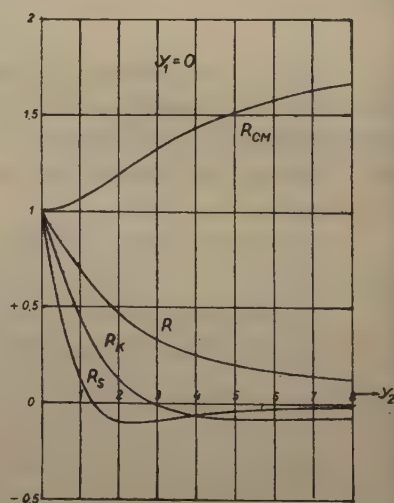


Fig. 14. Dependence of the reducing factors on y_2 , expressed by formulae (60)–(63) when $y_1=0$.

changes its sign. On the other hand the change of the sign of R_K is not in agreement with the experimental results.

From both these limiting cases we may now proceed to the general one, i. e. to the simultaneous existence of both kinds of coup-

ling. It has already been pointed out in §.7 that the dependance of y_1 on concentration is rather slight. Assuming y_1 to be constant and equal to unity and applying the general formulae for the reducing factors (32), (33), (34) and (45), we obtain the curves represented in fig. 15. At low concentration these curves correspond more closely to the experimental curves with the Lorentz field (fig. 1), than the curves in both limiting cases discussed above. But for higher concentration, the same differences between the theoretical and the ex-

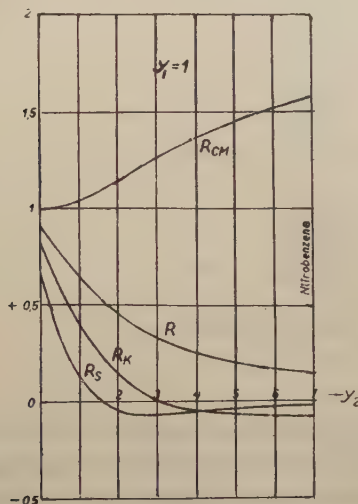


Fig. 15. Dependence of the reducing factors on y_2 , expressed by formulae (32), (33), (34) and (45) when $y_1 = 1$.

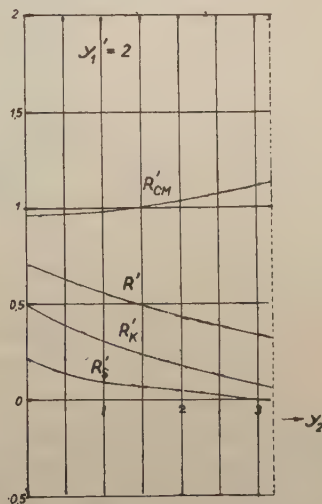


Fig. 16. The same reducing factors as in Fig. 15 calculated on the assumption that y_1 (now denoted by y_1') = 2. The interval of variation of y_2 reduced to (0—3.2).

perimental curves occur and these differences cannot be altered by changing the dependence of y_2 on n .

We should inquire then, whether or not there is any similarity between the theoretical curves in figs 4, 6, 8, 10 and the experimental ones based on the assumption that the Onsager field (fig. 2) exists. For this purpose set $y_1 = 2$ and reduce the interval of variation of y_2 so that y_2 shall not be greater than c. 3.2. The curves represented in fig. 16 are then obtained. (All the reducing factors hitherto used and y_1 will be denoted now with a dash to avoid confusion with the same factors to be introduced in the next section). If we now take into account the relation between y_2 and n (v. formula (55), curve fig. 12), the curves shown in fig. 17 will be obtained. Between these and the Onsager curves of fig. 2 a similarity exists for very low, but disappears

for stronger concentrations. This circumstance suggests the existence of a third kind of coupling. The tendency of the experimental curve for R_{CM} to rise shows that this new kind of coupling leads to the pro-

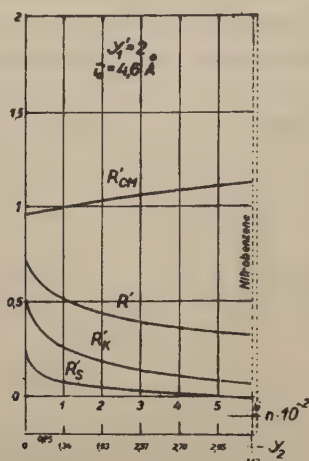


Fig. 17. n -dependence of the same reducing factors as in Fig. 15.

duction of larger aggregates with increased moment; this latter statement is proved by the fact that the curves R and R_K rise instead of falling. In the following we shall assume the existence of aggregates of two pairs (cf. Section 4).

§ 9. Third kind of coupling and comparison with experimental results. The theory of coupling assumes that all the molecular dipoles of the solution or of the pure liquid are coupled in pairs. A certain mean value of the coupling energy y_2 corresponds to each pair. Besides, each molecule is subjected to the coupling of the first kind with a value of the coupling energy y_1 . Owing to the diagrams in fig. 4, 6, 8 and 10 we are able to determine the reducing factors R' , R_K , R_s and R'_{CM} by which the molecular constants of the gas or vapour has to be multiplied in order to obtain the corresponding constants of the liquid:

$$\left. \begin{aligned} P^{\text{dip}'} &=_{\text{gas}} P^{\text{dip}} \cdot R', \\ K^{m'} &=_{\text{gas}} K^m \cdot R_K \text{ etc.} \end{aligned} \right\} \quad (64)$$

The polar liquid or its solution consists in the given scheme of an assembly of dipole pairs. In what follows these pairs will be treated in the same manner as the molecules in the preceding sections, which

will, of course, give only a rough approximation to the real conditions. We shall denote the mean energy of coupling into double pairs by y_3 . The single pairs are also subject to the coupling of the first kind with a coupling energy which we shall denote by y'_1 . For every pair of variables y'_1 and y_3 we calculate the corresponding reducing factors R'' , R'_K , R'_s and R'_{CM} . If the pairs are coupled nearly parallel as was assumed for the case of nitrobenzene, the reducing factors must be found from the diagrams in fig. 5, 7, 9 and 10.

Finally, the molecular constants will be given by

$$\left. \begin{aligned} P^{\text{dip}} &= P^{\text{dip}'} R'' = {}_{\text{gas}} P^{\text{dip}} \cdot R' \cdot R'', \\ K^m &= K^{m'} R'_K = {}_{\text{gas}} K^m \cdot R'_K \cdot R'_K \text{ etc.} \end{aligned} \right\} \quad (65)$$

and the reducing factors for the molecular constants $\left(R = \frac{P^{\text{dip}}}{{}_{\text{gas}} P^{\text{dip}}} \text{ etc.} \right)$ will be

$$\left. \begin{aligned} R &= R' R'', \\ R_K &= R'_K \cdot R''_K, \\ R_s &= R'_s \cdot R''_s, \\ R_{CM} &= R'_{CM} \cdot R''_{CM}. \end{aligned} \right\} \quad (66)$$

As in the case of y'_1 we neglect the variation of y'_1 with concentration in comparison with the strong n -dependence of y_3 . It remains to calculate the latter.

In order to calculate y_3 as function of the concentration we must make our simplified scheme somewhat more precise. A solution containing n dipoles per c. c. consists of $\frac{n}{2}$ pairs. Some of these pairs are very slightly coupled, others so strongly that they may be regarded as rigid, but the coupling of the third kind can only take place between pairs which are „rigid enough“.

Now, the number n' of these „rigid enough“ pairs per c. c. of the solution will be calculated. A „rigid enough“ pair will mean a pair both of whose molecules are separated by a distance not greater than a certain r' and whose axes include an angle not greater than Θ_2 ; moreover $r_0 < r' < R$, where R is determined by formula (48) and $0 < \Theta_2 < \frac{\pi}{2}$. Calculate the number n' of the „rigid enough“ pairs per c. c. by a method similar to that used for dn' in (51), expressing p by formula (50). This gives:

$$\begin{aligned}
 n' &= \frac{n}{2} \frac{\int_{r_0}^R r^2 dr \int_0^{\theta_2'} e^{-\frac{u}{kT}} \sin \theta_2 d\theta_2}{\int_{r_0}^R r^2 dr \int_0^{\pi} e^{-\frac{u}{kT}} \sin \theta_2 d\theta_2} \\
 &= \frac{n}{2} \frac{A}{\int_{r_0}^R r^5 \sinh \frac{a}{r} dr},
 \end{aligned} \tag{67}$$

where A is a certain constant.

Assume now that two „rigid enough“ pairs are able to unite only when approaching one another to a very small distance and neglect the volume of the molecules and the Boltzman factor (which cannot play a significant part in the case of nearly antiparallel pairs, i. e., of pairs with very small resulting moment). Then the probability p' of forming a double pair can be considered to be proportional to n' :

$$p' = Bn', \tag{68}$$

where B is a constant independent of the concentration. If the number of „rigid enough“ pairs is increased by dn' , the number of double pairs n'' increases by

$$dn'' = Bn' dn'$$

and hence

$$n'' = \frac{1}{2} Bn'^2. \tag{69}$$

The mutual energy of two „rigid enough“ pairs coupled into a double pairs is expressed by formula (25):

$$U_3 = -W_3 \cos \theta_3,$$

where W_3 is the energy of coupling of the double pair. The whole energy of coupling in double pairs for all molecules attains therefore the value of $W_3 n''$. In a solution of n dipole molecules per c. c. there exist $\frac{n}{2}$ more or less strongly coupled pairs. If we imagine, as in our simplified scheme, that all the pairs are subjected to a coupling of the third kind, $\frac{n}{4}$ double pairs would be created and for each pair

a certain mean coupling energy \bar{W}_3 would exist, given by the formula

$$\bar{W}_3 = \frac{W_3 n''}{\frac{n}{4}} = \frac{A^2 B W_3}{2} \cdot \frac{n}{\left(\int_{r_0}^R r^5 \sin h \frac{a}{r^3} dr \right)^2}.$$

This mean coupling energy measured in kT -units is therefore

$$y_3 = \frac{\bar{W}_3}{kT} = C \frac{n}{\left(\int_{r_0}^R r^5 \sin h \frac{a}{r^3} dr \right)^2}, \quad (70)$$

where $C = \frac{A^2 B W_3}{2kT}$ is independent of the concentration. The experimental results compel us to assume for C the minute value of $3,5 \times 10^{-108}$ and for the coupling energy of the first kind $y_1'' = 1$. With this value of the constant C the variation of y_3 with the concentration n is represented by the curve in fig. 18. We see that in dilute solutions the coupling of the third kind does not play any significant part and its influence becomes apparent only at higher concentrations. The reducing fac-

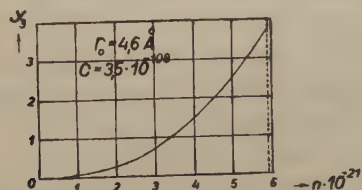


Fig. 18. Variation of the coupling energy of the third kind with n .

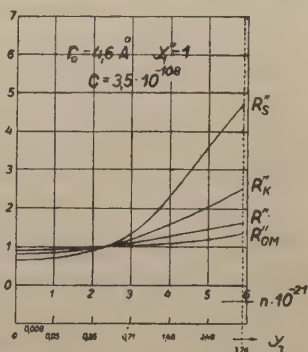


Fig. 19. Reducing factors R'' , R''_K , R''_s and R''_{CM} for double pairs coupled in a nearly parallel way.

tors R'' , R''_K , R''_s and R''_{CM} taken from the curves in Figs 5, 7, 9 and 10 for $y_1'' = 1$ and for different values y_3 from formula (70) are represented graphically in Fig. 19 as functions of the concentration. Finally, the reducing factors R , R_K , R_s and R_{CM} being products of factors from diagrams 17 and 19, are represented in Fig. 20.

The similarity of the theoretical curves in Fig. 20 with the experimental curves in fig. 2 calculated on the assumption of the Onsager

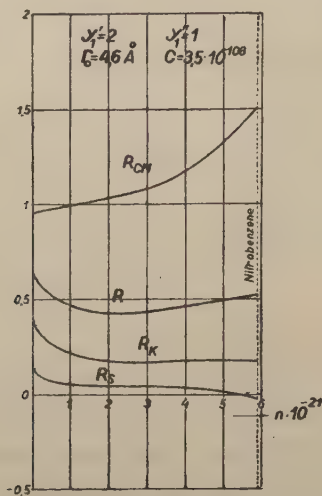


Fig. 20. Final results: reducing factors calculated on the assumption of the existence of a coupling of the first kind ($y'_1=2$), of the second kind (y_2 varying according to Fig. 12) and of the third kind ($y'_1=1$, y_3 varying as shown in Fig. 18). To be compared with the reducing factors calculated from experimental data assuming the existence of an Onsager local field, Fig. 2.

field is evident. The following similarities and differences are of interest:

(1) For an infinitely diluted solution ($n=0$) the reducing factors obtained, which give the rate „of coupling with the solvent“ are represented in the following table

Reducing factors of molar constants for $n=0$

Phenomenon	Experimental (Onsager's field)	Theoretical ($y'_1=2$, $y''_2=1$)
Dielectric polarization	c. 0,66	0,64
Kerr effect	c. 0,4	0,40
Electric saturation	c. 0,17	0,15
Cotton-Mouton effect ⁴	1	0,96

⁴ The value 1 has not been calculated from the experimental value of the Cotton-Mouton constant $_{\text{gas}}O^m$ of nitrobenzene vapour (as such a value does not exist) but has been obtained by extrapolation of O^m of nitrobenzene in solution for $n=0$. It is hoped that the error thus introduced is only insignificant.

We see that the agreement is very satisfactory. It cannot be obtained when the Lorentz field is assumed (cf. the diagrams in Figs 1 and 15).

(2) For small concentrations the graphs of all theoretical curves are in rather good agreement with the graphs of the experimental curves: R , R_K , R_s fall, while R_{CM} rises.

(3) For middle concentrations R_{CM} and R_K are too low compared to the experimental curves. On the other hand, there is a striking similarity in the way curves R , R_K and R_s cease falling and continue horizontally both in the theoretical and experimental graphs.

(4) In the region of strong concentrations the theoretical curve R_K begins to fall slightly instead of rising. On the other hand the curves R and R_s are in accord with experiment. Especially striking is the similarity of the two curves R_s , which are almost straight for most of the graph, and which give a change of sign of the ordinate for a concentration of about $n = 5,2 \cdot 10^{21}$.

It is worth while to point out the fact that the agreement between theory and experiment was obtained simultaneously for four very different phenomena. This was attained by a set of four constants, of which only three are completely arbitrary, namely $y'_1 = 2$, $y''_1 = 1$ and $C = 3,5 \times 10^{-108}$. On the other hand the fourth constant $r_0 = 4,6 \text{ \AA}$ has a value restricted between rather narrow limits.

The fact that the theory of dipole coupling leads to curves, which both by their position and their course show a similarity to the experimental curves seems to indicate that the generalized Onsager's conception of a local field represents reality better than the Lorentz field and that the coupling of the first, second and third kinds represent rather well the character of the mutual intermolecular influences between polar molecules in non-polar solvents.

I take great pleasure in thanking Professor H. Fröhlich for interesting discussions and valuable remarks.

Note added in proof. The reducing factor for dielectric polarization of nitrobenzene was calculated by Oster (1946) from measurements of ϵ_{12} and d_{12} in nitrobenzene-hexane mixtures. He applies the Onsager-Kirkwood theory (Kirkwood 1939- cf. Frenkel 1946) in a form with a semi-empirical reducing factor called "correlation parameter". This theory leads in the case of polar molecules in non-polar solvents to the formula (2) and (3) in Oster's paper, which we rewrite using our notations, as follows

$$\frac{\epsilon_{12}-1}{3g_{12}} \frac{M_{12}}{d_{12}} = P_1 f_1 + \left[P_2^n + \frac{P_{\text{gas}}^{\text{dip}} R}{(1-r_{12} p_1)^2} \right] f_2.$$

This formula is similar to our formulae (36) Part I and (19) Part II. The difference lies in factors $\frac{1}{1-r_{12} p_{1,2}}$, which is due to incorrect calculation of the mo-

ment of torque acting on a molecule in the original theory of Onsager (cf. Part I, p. 42), which has influenced the Kirkwood-Oster formula. Nevertheless, the general behaviour of the reducing factor as function of concentration is in Oster's paper similar to that in the present work (see Part I, Fig. 1 curve for $k=1$). A major difference refers to pure nitrobenzene for which, according to Oster, $R>1$, while our calculation gives $R \cong 0.5$. Oster concludes that nitrobenzene molecules, in spite of antiparallel association at low concentrations, show a tendency to parallel arrangement of their dipoles at large concentrations. This supposition, however, is inconsistent with the extensive experimental material presented here as well as with the assumptions of the theory outlined in this paper.

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THE SELF-ENERGY OF SCALAR MESONS IN INTERACTION WITH NUCLEI

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The meson self-energy is calculated using the scalar and scalar-product coupling. In the second case the self-energy operator contains derivatives of the meson fields. It is shown that this operator can be removed by changing the transformation function from the Schroedinger to the interaction representation and that this change is equivalent to a change in mass, i. e. to a mass renormalization.

In a series of papers Schwinger (1948, 1949) has shown, by means of a new, Lorentz-invariant formulation of quantum electrodynamics, that all the divergent integrals there encountered may be interpreted as either mass or charge renormalization effects. Kanesawa and Tomonaga (1948) and Miyamoto (1948) have given the means by which to extend the Tomonaga-Schwinger formalism to other fields, e. g. the various meson fields. In all cases, however, where the interaction terms of the Hamiltonian contain derivatives of the field operators, the renormalization is not as straightforward as in electrodynamics (Case 1949).

We shall investigate in this paper the simplest case of charged scalar mesons interacting with nuclei. There are two kinds of interactions possible, one of which contains derivatives of the meson field. This part gives rise to a self-energy operator which cannot immediately be recognized as a mass-renormalization effect. It can be shown, however, that up to the second order approximation we can remove this term by changing the transformation function from the Schroedinger to the interaction representation. This change in the transformation function is shown to cause a change in the mass of the meson.

In the first paragraph we shall briefly derive a part of the formalism already contained in a more general form in the work of the Japanese authors. In the second paragraph we shall calculate the self-energy terms of the meson field. Finally third paragraph contains the interpretation of the results.

§ 1. The Interaction Hamiltonian. We start with a Lagrangean:

$$L = L_m + L_n + L_i, \quad (1)$$

where

$$L_m = -\frac{\partial \varphi^*}{\partial x_\nu} \cdot \frac{\partial \varphi}{\partial x_\nu} - \kappa_m^2 \varphi^* \varphi, \quad (2)$$

$$L_n = -\bar{\psi}_N \left(\gamma_\nu \frac{\partial}{\partial x_\nu} + \kappa_N \right) \psi_N - \bar{\psi}_P \left(\gamma_\nu \frac{\partial}{\partial x_\nu} + \kappa_P \right) \psi_P. \quad (3)$$

Here m, n, i, N, P denote meson, nucleon, interaction, neutron and proton respectively.

Units are chosen in which $\hbar = c = 1$. The notation for the spinor field is exactly the same as in Schwinger's Part I. The two simplest invariants give the interaction term (Kemmer 1938):

$$L_i = -\bar{\psi}_N \left(g \varphi^* + f \gamma_\nu \frac{\partial \varphi^*}{\partial x_\nu} \right) \psi_P - \bar{\psi}_P \left(g^* \varphi - f^* \gamma_\nu \frac{\partial \varphi}{\partial x_\nu} \right) \psi_N. \quad (4)$$

g and f are coupling constants. The corresponding Hamiltonian is obtained by the usual methods.

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i, \quad (5)$$

where

$$\mathcal{H}_0 = \mathcal{H}_n + \mathcal{H}_m, \quad (5')$$

is the sum of the Hamiltonians of the free particles, and

$$\begin{aligned} \mathcal{H}_i = & g \varphi^* \cdot \bar{\psi}_N \psi_P + f \frac{\partial \varphi^*}{\partial x_i} \bar{\psi}_N \gamma_i \psi_P - i f \pi \bar{\psi}_N \gamma_4 \psi_P \\ & + g^* \varphi \cdot \bar{\psi}_P \psi_N - f^* \frac{\partial \varphi}{\partial x_i} \bar{\psi}_P \gamma_i \psi_N + i f^* \pi^* \bar{\psi}_P \gamma_4 \psi_N + |f|^2 \bar{\psi}_N \gamma_4 \varphi_P \cdot \bar{\psi}_P \gamma_4 \psi_N \end{aligned} \quad (6)$$

is the interaction part of the Hamiltonian. π, π^* are the momenta conjugate to φ^*, φ . The suffix i denotes summation over the indices 1, 2, 3 only. The Schroedinger equation is

$$i \frac{\partial \Psi}{\partial t} = \int \mathcal{H}(\vec{x}) d\vec{x}. \quad (7)$$

We transform this equation to the interaction representation by means of the transformation:

$$\Phi = e^{iH_0 t} \Psi. \quad (8)$$

The new state function satisfies the equation:

$$i \frac{\partial \Phi}{\partial t} = e^{iH_0 t} \{H - H_0\} e^{-iH_0 t} \equiv H' \Phi \quad (9)$$

where

$$H \equiv \int \mathcal{H}(\vec{x}) d\vec{x}, \quad H_0 \equiv \int \mathcal{H}_0(\vec{x}) d\vec{x}, \quad H' \equiv \int \mathcal{H}'(\vec{x}, t) d\vec{x}. \quad (10)$$

The operators in the interaction representation are now time dependent and are connected with the time-independent operators of the Schrödinger representation by means of the formula

$$0(\vec{x}, t) \equiv 0(x) = e^{iH_0 t} 0(\vec{x}) e^{-iH_0 t} \quad (11)$$

\mathcal{H}' is now the same function of the new operators as \mathcal{H}_i was of the old ones (6). From (11) and (5'), using the explicit expression for \mathcal{H}_m :

$$\mathcal{H}_m \equiv \pi^* \pi + \frac{\partial \varphi^*}{\partial x_i} \frac{\partial \varphi}{\partial x_i} + \kappa_m^2 \varphi^* \varphi. \quad (12)$$

we easily obtain:

$$\begin{aligned} \pi(x) &= \dot{\varphi}^*(x) \\ \pi^*(x) &= \dot{\varphi}(x) \end{aligned} \quad (13)$$

The \mathcal{H}' in (9) becomes, therefore, simply

$$\begin{aligned} \mathcal{H}'(x) &= \bar{\psi}_N \left(g \varphi^* + f \gamma_\nu \frac{\partial \varphi^*}{\partial x_\nu} \right) \psi_P + \bar{\psi}_P \left(g^* \varphi - f^* \gamma_\nu \frac{\partial \varphi}{\partial x_\nu} \right) \psi_N \\ &+ |f|^2 \bar{\psi}_N \gamma_4 \psi_P \cdot \bar{\psi}_P \gamma_4 \psi_N. \end{aligned} \quad (14)$$

The transition from (9) to the Tomonaga-Schwinger equation

$$i \frac{\delta \Phi[\sigma]}{\delta \sigma(x)} = \mathcal{H}' \Phi[\sigma] \quad (15)$$

is as yet impossible because the compatibility condition for this equation

$$\left[\frac{1}{i} \frac{\delta}{\delta \sigma(x)} + \mathcal{H}'(x), \frac{1}{i} \frac{\delta}{\delta \sigma(x')} + \mathcal{H}'(x') \right] = 0 \quad \text{for } (x_\mu - x'_\mu)^2 > 0 \quad (16)$$

is not fulfilled. In (15) and (16) $\sigma(x)$ is an arbitrary space-like surface through the point x , $\varphi[\sigma]$ is a functional of this surface and

$$\frac{\delta \Phi[\sigma]}{\delta \sigma(x)} = \lim_{\sigma' \rightarrow \sigma} \frac{\Phi[\sigma'] - \Phi[\sigma]}{d\omega} \quad (17)$$

In (17) σ' differs from σ only in the neighbourhood of x and ω is the four-dimensional volume element enclosed by the two surfaces.

Kanesawa and Tomonaga (1948) have given a very general method of dealing with such problems¹. To \mathcal{H} a term is added, depending on the point x and on the surface σ through x . This term is then determined by condition (16) and by the requirement that it vanishes for $\sigma(x)=\text{const}$. It proves, furthermore, that such a term brings the interaction Hamiltonian to an invariant form. In our case a simple but tedious calculation, carried out by means of the commutation laws given in the next paragraph, yields for the new Hamiltonian:

$$\mathcal{H}[x\sigma] = \bar{\psi}_N \left(g\varphi^* + f\gamma_\nu \frac{\partial \varphi^*}{\partial x_\nu} \right) \psi_P + \bar{\psi}_P \left(g^*\varphi - f^*\gamma_\nu \frac{\partial \varphi}{\partial x_\nu} \right) \psi_N - |f|^2 \bar{\psi}_N \gamma_\mu N_\mu \psi_P \cdot \bar{\psi}_P \gamma_\nu N_\nu \psi_N. \quad (18)$$

Here N_μ is the unit vector normal to σ at the point x . For

$$\sigma = \text{const.} \quad N_i = 0, \quad N_4 = 1/i,$$

so that (18) goes over into (14), as required.

§ 2. Meson Self-Energy. The first two terms in (18) correspond to virtual processes and, therefore, must be removed by a transformation. This can be done by means of the transformation

$$\Phi[\sigma] \rightarrow e^{-iS[\sigma]} \Phi[\sigma] \quad (19)$$

$$\frac{\delta S[\sigma]}{\delta \sigma(x)} = \mathcal{H}'_1(x) = \bar{\psi}_N \left(g\varphi^* + f\gamma_\nu \frac{\partial \varphi^*}{\partial x_\nu} \right) \psi_P + \bar{\psi}_P \left(g^*\varphi - f^*\gamma_\nu \frac{\partial \varphi}{\partial x_\nu} \right) \psi_N. \quad (20)$$

If we denote

$$\mathcal{H}'_2[x\sigma] = -|f|^2 \bar{\psi}_N \gamma_\mu N_\mu \psi_P \cdot \bar{\psi}_P \gamma_\nu N_\nu \psi_N, \quad (21)$$

we obtain for the transformed equation (15), in the first order of approximation:

$$i \frac{\delta \Phi[\sigma]}{\delta \sigma(x)} = \mathcal{H}[x\sigma] \Phi[\sigma] = \left\{ \mathcal{H}'_2[x\sigma] + \frac{i}{2} [S[\sigma], \mathcal{H}'_1(x)] \right\} \Phi[\sigma]. \quad (22)$$

We emphasize that (22) is an approximate equation insofar as it contains only terms proportional to the squares of the coupling constants. All terms with higher powers are neglected. (20) may be integrated and yields

$$S[\sigma] = \int_{-\infty}^{\sigma} \mathcal{H}'_1(x) d\omega. \quad (23)$$

¹ A different and simpler method has been given recently by Matthews (1949).

Now we are only interested in processes in which the final state is the same as the initial state. This is the case if

$$\int_{-\infty}^{+\infty} \mathcal{H}_1(x) d\omega = 0. \quad (24)$$

Condition (24) enables us to rewrite (23)

$$S[\sigma] = \frac{1}{2} \int_{-\infty}^{+\infty} \mathcal{H}_1(x') \varepsilon[\sigma\sigma'] d\omega' \quad (25)$$

with

$$\begin{aligned} \varepsilon[\sigma\sigma'] &= 1 & \text{for } \sigma' \text{ later than } \sigma' \\ \varepsilon[\sigma\sigma'] &= -1 & \text{,, } \sigma \text{ ,, ,, } \sigma. \end{aligned} \quad (26)$$

Denoting for simplicity:

$$\begin{aligned} v &= \bar{\psi}_N \psi_P & v^* &= \bar{\psi}_P \psi_N \\ j_\nu &= \bar{\psi}_N \gamma_\nu \psi_P & -\tilde{j}_\nu^* &= \bar{\psi}_P \gamma_\nu \psi_N \end{aligned} \quad (27)$$

and using (25), (21) and (20), we may write down the new Hamiltonian occuring in (22) explicitly:

$$\begin{aligned} \mathcal{H}[x\sigma] &= |f|^2 j_\nu \tilde{j}_\mu^* N_\nu N_\mu \\ &+ \frac{i}{4} \int_{-\infty}^{+\infty} \left[g\varphi^{*'} v' + g^* \varphi' v^{*'} + f \frac{\partial \varphi^{*'}}{\partial x_\nu} j'_\nu + f^* \frac{\partial \varphi'}{\partial x_\nu} \tilde{j}_\nu^{*'} \right. \\ &\left. g\varphi^* v + g^* \varphi v^* + f \frac{\partial \varphi^*}{\partial x_\mu} j_\mu + f^* \frac{\partial \varphi}{\partial x_\mu} \tilde{j}_\mu^* \right] \varepsilon[\sigma\sigma'] d\omega'. \end{aligned} \quad (28)$$

The primed quantities are taken at the point x' .

To evaluate (28) we need commutation rules for the operators. According to (11) the operators in the interaction representation satisfy the force-free field equations. The commutation rules are, therefore, simply the well known rules for free fields:

$$\begin{aligned} \{\psi_N^\alpha(x), \bar{\psi}_N^\beta(x')\} &= \frac{1}{i} S_{\alpha\beta}(x-x') = \frac{1}{i} \left(\gamma_\nu \frac{\partial}{\partial x_\nu} - \kappa_N \right)_{\alpha\beta} \Delta(x-x'), \\ \{\psi_P^\alpha(x), \bar{\psi}_P^\beta(x')\} &= \frac{1}{i} S_{\alpha\beta}(x-x'), \quad \{a, b\} = ab + ba, \\ [\varphi(x), \varphi^*(x')] &= [\varphi^*(x), \varphi(x')] = i\Delta(x-x'). \end{aligned} \quad (29)$$

All other quantities either anticommute or commute. With the help of (29) we can write (28) as follows:

$$\mathcal{H}[x\sigma] = |f|^2 j_\nu \tilde{j}_\mu^* N_\nu N_\mu + \frac{i}{4} \int_{-\infty}^{\infty} \left\{ |g|^2 (\varphi^{*'} \varphi[v', v^*] + \varphi' \varphi^*[v^{*'}, v] - i\Delta(x-x') (v^* v' + v v^{*'})) \right. \\ \left. + |f|^2 \left(\frac{\partial^2 \varphi^{*'} \varphi}{\partial x'_\nu \partial x_\mu} [j'_\nu, \tilde{j}_\mu^*] + \frac{\partial^2 \varphi' \varphi^*}{\partial x'_\nu \partial x_\mu} [\tilde{j}_\nu^{*'}, j_\mu] - i \frac{\partial^2 \Delta(x-x')}{\partial x'_\nu \partial x_\mu} (\tilde{j}_\mu^* j'_\nu + j_\mu \tilde{j}_\nu^{*'}) \right) \right\} \varepsilon[\sigma\sigma'] d\omega'. \quad (30)$$

We have omitted the mixed terms proportional to f^*g or fg^* respectively because they give no contribution if κ_N is assumed equal to κ_P , as may be easily shown by calculations similar to those which follow.

(30) describes all second order processes in which the final state is the same as the initial state. We are, however, interested only in meson self-energy and, therefore, in processes in which the initial and final states consist of one meson and no nucleons. We call that part of (30) which gives a contribution to these processes the one-meson part of $\mathcal{H}[x\sigma]$ and denote it by $(\mathcal{H}[x\sigma])_{1\mu}$. Terms which do not contain the meson field operators drop out. In the remaining terms we have to take vacuum expectation values of quantities containing the nucleon operators. Thus

$$(\mathcal{H}[x\sigma])_{1\mu} = \frac{i|g|^2}{4} \int_{-\infty}^{+\infty} \left\{ (\varphi^{*'} \varphi)_{1\mu} \langle [v', v^*] \rangle_0 + (\varphi' \varphi^*)_{1\mu} \langle [v^{*'}, v] \rangle \right\} \varepsilon[\sigma\sigma'] d\omega' \\ + \frac{i|f|^2}{4} \int_{-\infty}^{+\infty} \left\{ \frac{\partial^2 (\varphi^{*'} \varphi)_{1\mu}}{\partial x'_\nu \partial x_\mu} \langle [j'_\nu, \tilde{j}_\mu^*] \rangle_0 + \frac{\partial^2 (\varphi' \varphi^*)_{1\mu}}{\partial x'_\nu \partial x_\mu} \langle [\tilde{j}_\nu^{*'}, j_\mu] \rangle_0 \right\} \varepsilon[\sigma\sigma'] d\omega'. \quad (31)$$

Here $(\varphi^{*'} \varphi)_{1\mu} = (\varphi^{*'} \varphi - \langle \varphi^{*'} \varphi \rangle_0)$. This means that in (31) we have singled out the one-particle effects by subtracting the possible non-vanishing vacuum effects. The commutators in (31) can be evaluated by means of (29) and (27):

$$[v' v^*] = \frac{1}{i} \{ \bar{\psi}_N S_P(x' - x) \psi_N - \bar{\psi}_P S_N(x - x') \psi'_P \} \\ [j'_\nu \tilde{j}_\mu^*] = \frac{1}{i} \{ \bar{\psi}_P \gamma_\mu S_N(x - x') \gamma_\nu \psi'_P - \bar{\psi}_N \gamma_\nu S_P(x' - x) \gamma_\mu \psi_N \} \quad (32)$$

The vacuum expectation value for the bilinear form occurring in (32) is

$$\langle \bar{\psi}'_\beta \psi_\alpha \rangle_0 = \frac{1}{i} S_{\alpha\beta}^{(-)}(x - x') \quad (33)$$

with

$$S^{(-)}(x-x') = \left(\gamma_v \frac{\partial}{\partial x_v} - \kappa \right) \Delta^{(-)}(x-x') \quad (34)$$

where

$$\Delta^{(-)} = \frac{1}{2}(\Delta + i\Delta^{(1)}) \quad (35)$$

$$\Delta(x) = -\frac{i}{(2\pi)^3} \int e^{ik_\mu x_\mu} \delta(k_\mu^2 + \kappa^2) \varepsilon(k) dk \quad (36)$$

$$\Delta^{(1)}(x) = \frac{1}{(2\pi)^3} \int e^{ik_\mu x_\mu} \delta(k_\mu^2 + \kappa^2) dk \quad (37)$$

$\varepsilon(k)$ is $+1$ or -1 depending on whether k_0 is positive or negative. From (33), (34) and (35) and assuming for simplicity $\kappa_N = \kappa_P = \kappa_n$ (this assumption makes no essential change in the formulae) we obtain for (32)

$$\langle [v'v^*] \rangle_0 = -4i \left\{ \frac{\partial \Delta}{\partial x_v} \frac{\partial \Delta^{(1)}}{\partial x_v} - \kappa_n^2 \Delta \Delta^{(1)} \right\} (x-x') \quad (38)$$

$$\langle [j'_v \tilde{j}_\mu^*] \rangle_0 = 4i \left\{ \frac{\partial \Delta}{\partial x_v} \frac{\partial \Delta^{(1)}}{\partial x_\mu} + \frac{\partial \Delta^{(1)}}{\partial x_v} \frac{\partial \Delta}{\partial x_\mu} - \delta_{\mu\nu} \left(\frac{\partial \Delta}{\partial x_\alpha} \frac{\partial \Delta^{(1)}}{\partial x_\alpha} + \kappa_n^2 \Delta \Delta^{(1)} \right) \right\} (x-x')$$

From the properties of the Δ - functions it follows that:

$$\begin{aligned} \langle [v^*v] \rangle_0 &= \langle [v'v^*] \rangle_0 \\ \langle [\tilde{j}_v^* j_\mu] \rangle_0 &= \langle [j'_v \tilde{j}_\mu^*] \rangle_0 \end{aligned} \quad (39)$$

and (31) becomes:

$$\begin{aligned} (\mathcal{H}[x\sigma])_{1\mu} &= \frac{i|g|^2}{4} \int_{-\infty}^{+\infty} \langle [v'v^*] \rangle_0 \varepsilon[\sigma\sigma'] (\varphi^{*'}\varphi + \varphi'\varphi^*)_{1\mu} d\omega' \\ &+ \frac{i|f|^2}{4} \int_{-\infty}^{+\infty} \langle [j'_v \tilde{j}_\mu^*] \rangle_0 \varepsilon[\sigma\sigma'] \frac{\partial^2}{\partial x'_v \partial x_\mu} (\varphi^{*'}\varphi + \varphi'\varphi^*)_{1\mu} d\omega' \\ &= |g|^2 \int_{-\infty}^{+\infty} G(\lambda) (\varphi^{*'}\varphi + \varphi'\varphi^*)_{1\mu} d\omega' \\ &+ |f|^2 \int_{-\infty}^{+\infty} F(\lambda) \frac{\partial^2}{\partial x'_\mu \partial x_\mu} (\varphi^{*'}\varphi + \varphi'\varphi^*)_{1\mu} d\omega'. \end{aligned} \quad (40)$$

The functions $G(\lambda)$ and $F(\lambda)$ are determined by (38). We are, however, not interested in their explicit form. The important fact which can be easily shown, is that they are functions of the scalar

$$\lambda = -(x_\mu - x'_\mu)^2. \quad (41)$$

It may also be noted that $F(\lambda)$ has the same form as in the problem of the foton self-energy. This is plausible because of the similarity of the problems.

To get the final form of our expressions we expand (40) in a Fourier-integral

$$\int G(\lambda) \varphi(x') d\omega' = \frac{1}{(2\pi)^3} \int d\omega' \int G(k^2) e^{ik_\mu(x_\mu - x'_\mu)} dk \cdot \int \varphi(k') e^{ik'_\mu x'_\mu} dk'.$$

Because of

$$(\square - \kappa_m^2) \varphi = 0$$

and because of the integration over x' ,

we have

$$k_\mu^2 = k'_\mu{}^2 = -\kappa_m^2,$$

and, therefore,

$$\int G(\lambda) \varphi(x') d\omega' = \frac{G(-\kappa_m^2)}{(2\pi)^4} \int dk \varphi(k) e^{ik_\mu x_\mu} = G(-\kappa_m^2) \varphi(x). \quad (42)$$

Analogously,

$$\int F(\lambda) \frac{\partial \varphi'}{\partial x'_\mu} d\omega' = F(-\kappa_m^2) \frac{\partial \varphi(x)}{\partial x_\mu}. \quad (43)$$

It is understood that $G(k^2)$ and $F(k^2)$ are the Fourier transforms of $G(\lambda)$ and $F(\lambda)$ respectively.

Using (42) and (43) we finally obtain

$$\begin{aligned} (\mathcal{H}[x\sigma])_{1\mu} &= |g|^2 G(-\kappa_m^2) (\varphi^* \varphi + \varphi \varphi^*)_{1\mu} \\ &+ |f| F(-\kappa_m^2) \left(\frac{\partial \varphi^*}{\partial x_\mu} \frac{\partial \varphi}{\partial x_\mu} + \frac{\partial \varphi}{\partial x_\mu} \frac{\partial \varphi^*}{\partial x_\mu} \right)_{1\mu}. \end{aligned} \quad (44)$$

§ 3. Interpretation. The first term in (44) can be considered as a mass renormalization factor in the usual way (Schwinger 1948). The same procedure, however, does not apply to the second term because it contains derivatives of the field-operators. It seems impossible to regard this term correctly as a mass renormalization factor. We must remember, however, that the whole procedure is valid only to terms of the second order in the coupling constant. It is sufficient, therefore, to find a procedure which enables us to regard the second term as approximately a mass renormalization effect up to terms of the order $|f|^2$. We must of course assume that the divergent integral

$F(-\kappa_m^2)$ is in some way cut off and, therefore, small. Under these assumptions if we write the second term of (44) in the form

$$\varepsilon \left(\frac{\partial \varphi^*}{\partial x_\nu} \frac{\partial \varphi}{\partial x_\nu} \right)_{1\mu} \quad (45)$$

we may regard the dimensionless constant

$$\varepsilon = 2|f|^2 F(-\kappa_m^2) \quad (46)$$

as small.

We can now rewrite the Hamiltonian (5) in the following way:

$$\mathcal{H}_m + \mathcal{H}_i = \mathcal{H}_m + \mathcal{H}_s + \mathcal{H}_i - \mathcal{H}_s \quad (47)$$

with

$$\mathcal{H}_s = \varepsilon \frac{\partial \varphi^*}{\partial x_i} \frac{\partial \varphi}{\partial x_i} - \frac{\varepsilon}{1+\varepsilon} \pi^* \pi. \quad (48)$$

We drop the nucleon Hamiltonian \mathcal{H}_n because it does not play any role in the following considerations. Instead of transformation (8) we now use

$$\Phi = e^{i(H_0 + H_s)t} \Psi \quad (49)$$

which yields

$$0(x) = e^{i(H_0 + H_s)t} 0(x) e^{-i(H_0 + H_s)t} \quad (50)$$

and

$$\frac{\partial 0(x)}{\partial t} = i[H_0 + H_s, 0(x)]. \quad (51)$$

With (12) and (48) this gives, for the new time-dependent operators:

$$\frac{\partial \varphi}{\partial t} = \frac{1}{1+\varepsilon} \pi^*; \quad \frac{\partial \pi^*}{\partial t} = (1+\varepsilon) \Delta \varphi - \kappa_m^2 \varphi \quad (52)$$

and analogous expressions for $\frac{\partial \varphi^*}{\partial t}$ and $\frac{\partial \pi}{\partial t}$.

From (52) we get the equations of motion

$$\left(\square - \frac{\kappa_m^2}{1+\varepsilon} \right) \varphi = 0 \quad \left(\square - \frac{\kappa_m^2}{1+\varepsilon} \right) \varphi^* = 0 \quad (53)$$

with the new mass

$$\frac{\kappa_m}{\sqrt{1+\varepsilon}}.$$

The transformed interaction Hamiltonian becomes, up to terms in $|f|^2$:

$$\begin{aligned} \mathcal{H}'[x_\sigma] = & \bar{\psi}_N \left(g \varphi^* + f \gamma_\nu \frac{\partial \varphi^*}{\partial x_\nu} \right) \psi_P + \psi_P \left(g^* \varphi - f^* \gamma_\nu \frac{\partial \varphi}{\partial x_\nu} \right) \psi_N \\ & - |f|^2 \bar{\psi}_N \gamma_\mu N_\mu \psi_P \cdot \bar{\psi}_P \gamma_\nu N_\nu \psi_N - 2|f|^2 F(-\kappa_m^2) \frac{\partial \varphi^*}{\partial x_\nu} \frac{\partial \varphi}{\partial x_\nu}. \end{aligned} \quad (54)$$

The commutability of this expression on two space-like points is also valid only approximately up to terms of the second order in the coupling constant.

(53) shows that $-\varepsilon\kappa_m^2$ may be regarded as a mass-renormalization

$$\delta\kappa_m^2 = -2|f|^2 \kappa_m^2 F(-\kappa_m^2) \quad (55)$$

Considering κ_m as the mechanical mass, we get for the experimentally observable mass κ_m^{exp} :

$$(\kappa_m^{\text{exp}})^2 = \kappa_m^2 + \delta\kappa_m^2. \quad (56)$$

If we are not concerned with the self-energy operator but only with its diagonal terms, the self-energy, we may, of course, get the result (56) by transition to the momentum space. Indeed, writing

$$\begin{aligned} \varphi(x) &= \varphi(k) e^{ik_\mu x_\mu} \\ \varphi^*(x) &= \varphi^*(k) e^{-ik_\mu x_\mu} \end{aligned} \quad (57)$$

we get

$$\varepsilon \left(\frac{\partial \varphi^*}{\partial x_\nu} \frac{\partial \varphi}{\partial x_\theta} \right)_{\text{d. e.}} = \varepsilon k_\nu^2 (\varphi^* \varphi)_{\text{d. e.}} = -\varepsilon \kappa_m^2 (\varphi^* \varphi)_{\text{d. e.}} \quad (58)$$

(d. e. indicates the diagonal elements of the operator). For the self-energy operator, however, for which we must replace (57) by infinite series or by integrals, this kind of procedure does not give any results and we have to use transformation (49).

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REMARKS ON SOME NON-LINEAR EFFECTS IN FIELD THEORY. I.

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The scattering of a neutral scalar particle by another particle of the same kind and the spontaneous breaking up of a neutral particle is studied in Part I under the assumption of an interaction with a complex scalar field. These problems are analogous to the scattering of light by light and to the spontaneous breaking up of photons. The calculations are based on the Feynman-Dyson technique of solving problems in quantum field theory. The calculation of the scattering of light by light (coupling with pseudoscalar charged particles) is in preparation by B. Średniawa and the author and will appear as Part II.

A remarkable feature of the quantized field theory is its departure from the principle of superposition for the field variables in spite of the linearity of the classical field equations which are subject to the procedure of quantization. Such non-linear effects (e. g. the scattering of light by light) are due to the circumstance that in the quantum theory, the light is coupled to the charged fields even in the absence of actual charged particles; consequently the vacuum fluctuations of charged fields influence the behaviour of photons. In order to preserve the conservation laws two primary colliding photons must produce at least two final photons, so that the lowest order in the perturbation treatment where the scattering of light by light occurs, is the fourth. The scattering in question is due to the interaction with charged fermions as well as with charged bosons. The effect due to fermions has been calculated recently by Feynman (see Dyson 1949) with the aid of his relativistically invariant technique of calculation. Our aim is to study the scattering cross-section due to the interaction with charged scalar and pseudoscalar mesons. The total cross-section (in the lowest order of approximation e^4) is simply the sum of the separate expressions for all the charged fields.

The non-linear effects appear, obviously, in any quantized field theory, not necessarily in quantum electrodynamics. Therefore, to study non-linear aspects in the field theory, we may start with a much

simpler case of two coupled scalar fields: a complex one ψ and a real one φ . We shall calculate first the scattering of a particle associated with φ by another particle of the same kind. For reasons of analogy with the light as well as for simplicity we shall assume a vanishing rest mass of these particles.

This comparatively simple problem is particularly suited to illustrate the modern technique developed by Feynman and Dyson (1949).

§ 1. The scattering between neutral particles. A scalar-scalar interaction energy density is:

$$h = f\psi^*\psi\varphi \quad (1)$$

where f means the coupling constant, ψ is the field variable of the complex field and φ that of the neutral field. In the interaction representation (Tomonaga 1946) (which we propose to call the „Tomonaga picture“) the field quantities obey the interaction-free Schrödinger-Klein-Gordon equations:

$$\begin{aligned} \square\psi - m^2\psi &= 0, & \square\psi^* - m^2\psi^* &= 0 \\ \square\varphi &= 0 \end{aligned} \quad (2)$$

and the invariant commutation relations:

$$[\psi(1), \psi^*(2)] = i\Delta(12); \quad [\varphi(1), \varphi(2)] = iD(12), \quad (3)$$

where 1, 2 denote in short the points x_1^μ, x_2^μ and (12) denotes the difference $x_1^\mu - x_2^\mu$. Δ and D are the well known Jordan-Pauli delta functions given by Schwinger (1949).

The Schroedinger equation may be written in an invariant form (Rayski 1950)

$$i \frac{d\Psi[\Sigma]}{d\Sigma} = \int_{\Sigma} d\Sigma h(P_{\Sigma}) \cdot \Psi[\Sigma], \quad (4)$$

where $\Psi[\Sigma]$ is a functional of the variable space-like hyperplane Σ while $\frac{d}{d\Sigma}$ means the normal functional derivative in respect to the plane Σ . (1)–(4) form an invariant basis describing the behaviour of the quantized fields ψ and φ . Equation (4) connects only those values of Ψ among themselves which refer to a set of parallel planes; hence, we may assume a system of reference with the time axis pointing in the direction of the normal to the plane Σ_0 (Σ_0 means that plane

where the initial state has been fixed by measurement). In this system of reference (4) assumes the simple form:

$$i \frac{d\Psi(t)}{dt} = H(t) \Psi(t) \quad (4')$$

with

$$H(t) = \int d^4x h(x, t). \quad (4'')$$

We assume a state fixed for $t \rightarrow -\infty$ by the statement that there exist two particles associated with the field φ with momenta k_1^μ, k_2^μ and no particles associated with the field ψ . We look for the probability of finding for $t \rightarrow +\infty$ two particles of the first kind with momenta k_3^μ, k_4^μ and, again, without any particles associated with ψ .

The elements of the S -matrix of Heisenberg (1943):

$$\Psi(\infty) = S\Psi(-\infty) = (1 + R) \Psi(-\infty) \quad (5)$$

responsible for the scattering in question are found by the usual perturbation treatment:

$$R = \int d^4x_1 \int d^4x_2 \int d^4x_3 \int d^4x_4 h(1) h(2) h(3) h(4) \quad (6)$$

$t_1 > t_2 > t_3 > t_4$

or

$$R = \frac{1}{4!} \int_{-\infty}^{+\infty} d^4x_1 \dots \int_{-\infty}^{+\infty} d^4x_4 P[h(1) h(2) h(3) h(4)], \quad (6')$$

where $P[ab\dots]$ means the product of the arguments arranged according to their time sequence. The integrations in (6') are extended over the whole space-time manifold. Due to the commutability of φ with ψ or ψ^* ,

$$P[h(1)h(2)\dots h(4)] = i^4 P[\psi^*(1)\psi(1)\psi^*(2)\psi(2)\dots\psi(4)] P[\varphi(1)\dots\varphi(4)] \quad (7)$$

The order of the φ functions in (7) is immaterial since any change in the order of φ 's yields, from (3), additional terms with a diminished number of φ 's which are immaterial for our scattering problem. Thus we may replace $P[\varphi(1)\dots\varphi(4)]$ by the product $\varphi(1)\varphi(2)\dots\varphi(4)$. Next, we have to take the vacuum expectation value $\langle P[\psi^*(1)\dots\psi(4)] \rangle_0$. Assume for a while that $t_1 > t_2 > t_3 > t_4$. In this case the operator $\langle P \rangle_0$ yields simply:

$$\langle \psi^*(1)\psi(1)\psi^*(2)\psi(2)\psi^*(3)\psi(3)\psi^*(4)\psi(4) \rangle_0$$

which may be written in the form

$$\begin{aligned} & \langle \psi^*(1)\psi(2) \rangle_0 \langle \psi(1)\psi^*(2) \rangle_0 \langle \psi(3)\psi^*(4) \rangle_0 \langle \psi^*(3)\psi(4) \rangle_0 \\ & + \langle \psi(1)\psi^*(2) \rangle_0 \langle \psi^*(1)\psi(3) \rangle_0 \langle \psi(2)\psi^*(4) \rangle_0 \langle \psi^*(3)\psi(4) \rangle_0 + \text{etc.}, \end{aligned}$$

where all the permutations of 1, 2, 3, 4 should be taken into account except the reversing of the order in the separate terms $\langle \psi(i)\psi^*(j) \rangle_0$ and $\langle \psi^*(i)\psi(j) \rangle_0$. With the aid of the formulae

$$\langle \psi(1)\psi^*(2) \rangle_0 = i\Delta^+(12), \quad \langle \psi^*(2)\psi(1) \rangle_0 = -i\Delta^-(12) \quad (8)$$

with Δ^\pm given by Schwinger (1949), and by introducing

$$\Delta_c(12) = \begin{cases} 2i\Delta^+(12) & \text{for } t_1 > t_2 \\ -2i\Delta^-(12) & \text{for } t_2 > t_1 \end{cases} \quad (9)$$

where $\Delta_c(12)$ is the so called causal function introduced by Stueckelberg (1948) and Feynman (see Dyson 1949) we find

$$\langle P \rangle_0 = \frac{1}{16} (\Delta_c(21)\Delta_c(12)\Delta_c(34)\Delta_c(43) + \Delta_c(12)\Delta_c(31)\Delta_c(24)\Delta_c(43) + \text{etc.}). \quad (10)$$

It is easily seen that for a sequence of interchanged time variables we obtain exactly the same expression (10) so that (10) applies to any sequence of $t_1 \dots t_4$. The terms in (10) may be divided into two groups: 1) those with at least one $\Delta_c(ii)$ or with a $\Delta_c(ij)$ appearing twice, 2) those with $\Delta_c(ij)$ appearing only once for every i and j ($i \neq j$). The terms of the first type do not contribute to the cross section except in the cases of $k^\mu = 0$ or $k_i^\mu || k_j^\mu$ and may be abandoned. There remain six terms of the second type. Due to the symmetry

$$\Delta_c(ij) = \Delta_c(ji)$$

these six terms may be reduced to three, whence.

$$R = \frac{f^4}{4!} \frac{1}{8} \int d^4x_1 \dots d^4x_4 \varphi(1) \dots \varphi(4) \{ \Delta_c(12)\Delta_c(23)\Delta_c(34)\Delta_c(41) + \Delta_c(12)\Delta_c(24)\Delta_c(43)\Delta_c(31) + \Delta_c(13)\Delta_c(32)\Delta_c(24)\Delta_c(41) \}. \quad (11)$$

In order to evaluate $R(k_1 k_2 | k_3 k_4)$ we introduce for $\varphi(1) \dots \varphi(4)$ plane waves:

$$A_{k_1} e^{ik_1^\mu x^\mu}, \quad A_{k_2} e^{ik_2^\mu x^\mu}, \quad A_{k_3}^* e^{-ik_3^\mu x^\mu}, \quad A_{k_4}^* e^{-ik_4^\mu x^\mu}.$$

This replacement should be done, of course, in all possible ways, the number of which is 4! We may, instead, fix the arrangement of plane waves but permute the variables of integration. Hence:

$$R(k_1 k_2 k_3 k_4) = \frac{f^4}{8} A_{k_1} A_{k_2} A_{k_3}^* A_{k_4}^* \int d^4x \dots d^4x_4 e^{i(k_1^\nu x_1^\nu + k_2^\nu x_2^\nu - k_3^\nu x_3^\nu - k_4^\nu x_4^\nu)} \times \{ \Delta_c(12)\Delta_c(23)\Delta_c(34)\Delta_c(41)_c + \Delta_c(12)\Delta_c(24)\Delta_c(43)\Delta_c(31) + \Delta_c(13)\Delta_c(32)\Delta_c(24)\Delta_c(41) \}. \quad (12)$$

Let us introduce the well known representation of the Δ_c function:

$$\Delta_c(x) = \frac{1}{(2\pi)^4} \frac{2}{i} \int_C d^4p e^{ip^\nu x^\nu} \frac{1}{p_\nu^2 + m^2} \quad (13)$$

where C means the integration in the complex plane of the variable p_0 above (below) the real axis in the neighbourhood of the pole $\sqrt{p^2 + m^2}$ ($-\sqrt{p^2 + m^2}$). This yields for (12):

$$\begin{aligned} R(k_1 k_2 | k_3 k_4) = & 2f^4 \left(\frac{1}{2\pi} \right)^{16} A_{k_1} A_{k_2} A_{k_3}^* A_{k_4}^* \int d^4x_1 \dots d^4x_4 \int d^4p_1 \dots d^4p_4 \\ & \frac{e^{i(k_1 x_1 + k_2 x_2 - k_3 x_3 - k_4 x_4)}}{(p_1^2 + m^2)(p_2^2 + m^2)(p_3^2 + m^2)(p_4^2 + m^2)} \\ & \times \left\{ e^{i[p_1(x_1 - x_2) + p_2(x_2 - x_3) + p_3(x_3 - x_4) + p_4(x_4 - x_1)]} \right. \\ & + e^{i[p_1(x_1 - x_2) + p_2(x_3 - x_4) + p_3(x_4 - x_3) + p_4(x_3 - x_1)]} \\ & \left. + e^{i[p_1(x_1 - x_3) + p_2(x_3 - x_2) + p_3(x_2 - x_4) + p_4(x_4 - x_1)]} \right\}, \end{aligned}$$

where $p_i x_i$ or p_i^2 has been written instead of $p_i^\nu x_i^\nu$ or $p_\nu p_\nu$ for brevity. Integration over the variables $x_1 \dots x_4$ yields four (four dimensional) delta functions which immediately allows further integrations over p_4, p_3 and p_2 so that we are left with:

$$\begin{aligned} R(k_1 k_2 k_3 k_4) = & 2f^4 A_{k_1} A_{k_2} A_{k_3}^* A_{k_4}^* \delta^{(4)}(k_1^\mu + k_2^\mu - k_3^\mu - k_4^\mu) \\ & \times \int d^4p \left\{ \frac{1}{[p^2 + m^2][(p - k_2)^2 + m^2][(p + k_3 - k_2)^2 + m^2][(p + k_1)^2 + m^2]} \right. \\ & + \frac{1}{[p^2 + m^2][(p - k_2)^2 + m^2][(p + k_4 - k_2)^2 + m^2][(p + k_1)^2 + m^2]} \\ & \left. + \frac{1}{[p^2 + m^2][(p + k_3)^2 + m^2][(p + k_3 - k_2)^2 + m^2][(p + k_1)^2 + m^2]} \right\} \quad (14) \end{aligned}$$

The delta function $\delta^{(4)}(k_1^\nu + k_2^\nu - k_3^\nu - k_4^\nu)$ appearing in (14) expresses the laws of conservation of energy and momentum. In (14) use has been made of the property $k_1^2 = k_2^2 = k_3^2 = k_4^2 = 0$. To evaluate the integrals in (14) we notice the fact that the integrals are of the form $\frac{1}{ABCD}$ which may be conveniently transformed by means of an identity:

$$\frac{1}{A_0 A_1 \dots A_n} = n! \int_0^1 dx_1 \int_0^{x_1} dx_2 \int_0^{x_2} dx_3 \dots \int_0^{x_{n-1}} dx_n \quad (15)$$

$$\{ (A_n - A_{n-1})x_n + (A_{n-1} - A_{n-2})x_{n-1} + \dots + (A_1 - A_0)x_1 + A_0 \}^{-(n+1)}.$$

In our special case we get for the integral in (14):

$$6 \int d^4 p \int_0^1 dx \int_0^x dy \int_0^y dz \\ \{ [p_\mu^2 + 2p_\mu(k_2^\mu(z-x) - k_3^\mu(y-x) - k_1^\mu(x-1)) + 2k_2^\mu k_3^\mu(y-x) + m^2] \}^{-4} \\ + [\text{an analogous term with } k_3 \text{ replaced by } k_4]^{-4} \\ + [\text{an analogous term with } k_3 \text{ replaced by } -k_2 \text{ and vice versa}]^{-4}.$$

We introduce new variables of integration:

$$w = x - z \quad v = x - y \quad u = 1 - x$$

and denote

$$R = f^4 \delta^{(4)}(k_1^\nu + k_2^\nu - k_3^\nu - k_4^\nu) A_{k_1} A_{k_2} A_{k_3}^* A_{k_4}^* \{r_1 + r_2 + r_3\}. \quad (16)$$

Then we get:

$$r_i(k_1 k_2 | k_3 k_4) = 12 \int d^4 p \int_0^1 du \int_0^{1-u} dv \int_v^{1-u} dw \frac{1}{(p_\mu^2 + 2p_\mu Q_i^\mu + P_i)^4} \quad (17)$$

where

$$Q_1^\mu = k_1^\mu u + k_3^\mu v - k_2^\mu w, \quad P_1 = m^2 - 2k_2^\mu k_3^\mu v \quad (17')$$

while r_2, P_2, Q_2^μ are obtained from $r_1 P_1, Q_1^\mu$, by the replacement $k_3 \rightarrow k_4$ and r_3, P_3, Q_3^μ are obtained from $r_1 P_1, Q_1^\mu$, by the replacement $k_3 \rightleftarrows -k_2$.

Denoting $p_\mu + Q_\mu = q_\mu$ we get

$$\int d^4 p (p_\mu^2 + 2p_\mu Q_\mu + P)^{-4} = \int d^4 q (q_\mu^2 + P - Q^2)^{-4} \\ = (P - Q^2)^{-2} \int d^4 p (p_\mu^2 + 1)^{-4} \quad (18)$$

The last integral should be evaluated along the same path as the integral in formula (13) and yields

$$\int d^4 p (p_\mu^2 + 1)^{-4} = \frac{i\pi^2}{6}.$$

Thus, we are left with

$$r_i(k_1 k_2 | k_3 k_4) = 2\pi^2 i \int_0^1 du \int_0^{1-u} dv \int_v^{1-u} dw (P_i - Q_i^\mu Q_i^\mu)^{-2} \quad (19)$$

or, by introducing (17'),

$$r_1(k_1 k_2 k_3 k_4) = 2i\pi^2 \int_0^1 du \int_0^{1-u} dv \int_v^{1-u} dw \quad (20)$$

$$\{2k_2^v(k_1^v u + k_3^v v)w - 2k_2^v k_3^v v - 2k_1^v k_3^v uv + m^2\}^{-2}.$$

This integral is convergent. The integrations over w and v are elementary while the last integration over u may be performed numerically.

For small values of k_1^v, k_2^v the integrand is approximatively m^{-4} and we get an isotropic scattering with

$$r = r_1 + r_2 + r_3 = \frac{i\pi^2}{m^4}. \quad (21)$$

§ 2. Spontaneous breaking up of neutral particles.

Another effect violating the principle of superposition is the spontaneous breaking up of neutral particles. In case of two interacting scalar fields we already find breaking up in the third order of approximation.

Assume for $t \rightarrow -\infty$ a state $\Psi(-\infty)$ consisting of a single neutral particle with momentum \vec{k}_1 . We look for the probability of finding two particles of the same kind with momenta \vec{k}_2 and \vec{k}_3 for $t \rightarrow +\infty$. The matrix element in question is in this case:

$$R = \frac{if^3}{3!} \int d^4x_1 d^4x_2 d^4x_3 P[h(1)h(2)h(3)]. \quad (22)$$

By taking the vacuum expectation value of the complex field ψ and noticing that the order of the φ 's is immaterial we get:

$$R = \frac{if^2}{4 \cdot 3!} \int d^4x_1 \dots d^4x_3 \varphi(1)\varphi(2)\varphi(3) \Delta_c(12) \Delta_c(23) \Delta_c(31) \quad (23)$$

or

$$R(k_1|k_2k_3) = \frac{i}{4} f^3 A_{k_1} A_{k_2}^* A_{k_3}^* \int d^4x_1 \dots d^4x_3 e^{i(k_1x_1 - k_2x_2 - k_3x_3)} \cdot \Delta_c(12) \Delta_c(23) \Delta_c(31). \quad (24)$$

Introducing representation (13) we get:

$$R(k_1|k_2k_3) = -2f^3 A_{k_1} A_{k_2}^* A_{k_3}^* \delta^{(4)}(k_1 - k_2 - k_3) r(k_1|k_2k_3) \quad (25)$$

where

$$r(k_1|k_2k_3) = \int_c d^4 p \{ [p^2 + m^2] [(p + k_2)^2 + m^2] [(p + k_2 + k_3)^2 + m^2] \}^{-1}. \quad (26)$$

Here p^2 has been written instead of $p^\nu p_\nu$ etc. for brevity. The energy and momentum are conserved if $|\vec{k}_1| = |\vec{k}_2| + |\vec{k}_3|$ and $\vec{k}_1 = \vec{k}_2 + \vec{k}_3$. By using (15) and noting that $k_1^2 = k_2^2 = \dots = k_3^2 = 0$ we easily find

$$r(k_1|k_2k_3) = 2 \int_0^1 dx \int_0^x dy \int_c d^4 p (p^2 + 2Q_\mu p_\mu + P)^{-3}, \quad (27)$$

where

$$Q_\mu = k_2^\mu(x - y) + k_3^\mu(1 - x) + k_2^\mu, \quad P = m^2 \quad (27')$$

or

$$r(k_1|k_2k_3) = 2 \int_0^1 dx \int_0^x dy \frac{1}{\lambda^2} \int_c \frac{d^4 q}{(q^2 + 1)^3} \quad (28)$$

with

$$\lambda^2 = P - Q^2 = m^2. \quad (28')$$

The integral along the part C yields

$$\int_c \frac{d^4 q}{(q^2 + 1)^3} = \frac{i\pi^2}{2}, \quad (29)$$

whence

$$r(k_1|k_2k_3) = \frac{i\pi^2}{2m^2}. \quad (30)$$

Thus, we find an isotropic probability, but different from zero, for the breaking up of neutral particles.

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ON A SYSTEM OF FIELDS FREE OF DIVERGENCES OF THE MASS-RENORMALIZATION TYPE

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It is shown that a system of four different fields consisting of one photon, one electron, one C -meson, and two charged scalar meson fields is free of divergences of the mass-renormalization type.

The application of the procedure of mass and charge renormalization (Schwinger 1948, 1949) has proved to be of great practical value, enabling the computation of several effects (magnetic moment of the electron, Lamb-shift, corrections to the Compton effect etc.). Nevertheless, from the mathematical point of view, the procedure of mass renormalization is unsatisfactory as long as the self masses are infinite. It is hoped that a considerable progress may be achieved (without any drastic departure from the traditional conception of fields nor from the Heisenberg-Pauli formalism of field quantization) by means of a completion of quantum electrodynamics by: (1) Introducing additional physical fields and (2) by some formal improvements in the technique of calculation. From the physical point of view, it seems plausible to demand that all the fields believed to occur in nature should be dealt with simultaneously, since the divergences of the mass renormalization type may be eliminated by mutual compensation. On the other hand, it seems indispensable at the present stage to introduce also some formal procedures for dealing with symbols like δ , Δ etc. to prevent ambiguity in the results. This concerns, above all, the meaning of the Fourier expansions of these functions (e. g. the order in which Fourier and other summations have to be performed).

It has been shown by Pais (1947) and, independently, by Sakata (1947) that the self energy of charged spinor particles may be removed by introducing an interaction with a neutral scalar meson (called cohesive forces meson or, briefly, C -meson). On the other hand,

Umesawa with his collaborators (1948), and independently, one of the present authors (Rayski 1948) have shown that the self mass of photons vanishes if the electromagnetic field is coupled with spinor as well as with pseudoscalar (or scalar) charged fields. Now, the question arises as to whether the divergences may be removed also from the remaining, above-mentioned, fields i. e. whether the self energy of the pseudoscalar charged meson will also be compensated by the C -meson and whether both parts of the self energy of a C -meson itself (due to the couplings with electrons and charged mesons) compensate to a finite value without introducing any further additional fields. With the aid of some formal rules concerning the order of operations on the symbols δ , $\bar{\Delta}$, Δ (1) etc. and their Fourier transforms, the answer to this question is positive. Thus, we possess a comparatively simple system of fields free of divergences of the mass renormalization type. Quantum electrodynamics constitutes the chief part of this closed system of mutually compensating fields.

I. Self mass of the C -meson. (a) *Coupling with a charged pseudoscalar (or scalar) meson.* We assume a real scalar field φ associated with the neutral particles (with the rest mass m) and a complex pseudoscalar (or scalar) field ψ , ψ^* associated with the charged particles (with the rest mass κ). In the interaction representation called henceforth the „Tomonaga picture“ the field variables satisfy the interaction-free Schrödinger-Gordon-Klein equations

$$(\square - m^2)\varphi = 0, \quad (\square - \kappa^2)\psi = 0 \quad (1)$$

and the commutation relations ¹

$$[\varphi, \varphi'] = i\Delta_m(x - x'), \quad [\psi, \psi^{*'}] = i\Delta_\kappa(x - x'), \quad (2)$$

while other commutators between φ , ψ and ψ^* vanish. The equation for the state functional is (Tomonaga 1946)

$$i \frac{\delta \Psi[\sigma]}{\delta \sigma(x)} = h' \Psi[\sigma], \quad (3)$$

where $\sigma(x)$ is a space-like surface through the point x_μ , h' is the interaction energy density. We make the simplest possible assumption:

$$h = f\psi^*\psi\varphi. \quad (4)$$

¹ The notation used here and in the following is the standard notation introduced by Schwinger in his series of papers (1948, 1949).

With the aid of a unitary transformation (Schwinger 1949 a)

$$\Psi[\sigma] = e^{-iS[\sigma]} \Phi[\sigma] \quad (5)$$

with

$$\frac{\delta S[\sigma]}{\delta \sigma(x)} = f \psi^* \psi \varphi \quad (5')$$

we transform away the virtual first order processes and obtain a new equation:

$$i \frac{\delta \Phi[\sigma]}{\delta \sigma(x)} = h(x) \Phi[\sigma] \quad (6)$$

where

$$h(x) = -\frac{if^2}{8} \int d^4 x' \varepsilon[\sigma \sigma'] (\{\varphi, \varphi'\} [\varrho, \varrho'] + [\varphi, \varphi'] \{\varrho, \varrho'\}) \quad (6')$$

with

$$\varrho = \psi^* \psi. \quad (6'')$$

To evaluate the self energy of the C -meson we have to take the „one C -meson part“ of (6').

$$h_{1c} = h_{\text{self}} = -\frac{if^2}{8} \int d^4 x' \varepsilon[\sigma \sigma'] \langle [\psi^* \psi, \psi^{*'} \psi']_0 \rangle \{\varphi_1 \varphi'_{1c}\}. \quad (7)$$

In the following we need the vacuum expectation values of bilinear expressions:

$$\begin{aligned} \langle \psi^* \psi' \rangle_0 &= -i \Delta_x^{(-)}(x' - x), & \langle \psi \psi^{*'} \rangle_0 &= i \Delta_x^{(+)}(x - x') \\ \langle \varphi \varphi' \rangle_0 &= i \Delta_m^{(+)}(x - x'), & \langle \{\varphi_1 \varphi'\} \rangle_0 &= \Delta_m^{(1)}(x - x'). \end{aligned} \quad (8)$$

By virtue of (2) and (8), expression (7) assumes a simple form²

$$h_{\text{self}} = -\frac{f^2}{4} \int d^4 x' \Delta_x \Delta_x^{(1)} \{\varphi_1 \varphi'\}. \quad (9)$$

We Fourier-analyse the field functions

$$\varphi = \int d^4 k \varphi(k) \delta(k_\mu^2 + m^2) e^{ik_\mu x_\mu} \quad (10)$$

and using the well known (Schwinger 1949 a) Fourier representations of $\bar{\Delta}$ and $\Delta^{(1)}$ we obtain from (9)

$$\begin{aligned} h_{\text{self}} &= \frac{-f^2}{4(2\pi)^7} \int d^4 x' \int d^4 k \int d^4 k' \int d^4 k'' \frac{\delta(k_\mu^2 + \kappa^2)}{k_\mu'^2 + \kappa^2} e^{i(k_\mu + k'_\mu)(x_\mu - x'_\mu)} \\ &\quad \times \{\varphi(x), \varphi(k'')\} \delta(k_\mu''^2 + m^2) e^{ik_\mu'' x_\mu} \\ &= \frac{-f^2}{8(2\pi)^3} \int d^4 k \int d^4 k' \left\{ \frac{\delta(k_\mu^2 + \kappa^2)}{k_\mu'^2 + \kappa^2} + \frac{\delta(k_\mu'^2 + \kappa^2)}{k_\mu^2 + \kappa^2} \right\} e^{i(k_\mu + k'_\mu)x_\mu} \\ &\quad \times \{\varphi(x), \varphi(k + k')\} \delta[(k_\mu + k'_\mu)^2 + m^2]. \end{aligned} \quad (11)$$

² The argument of the Δ -functions under the integrals is $x_\mu - x'_\mu$.

We introduce

$$k_\mu = q_\mu + p_\mu, \quad k'_\mu = q_\mu - p_\mu, \quad (12)$$

whence

$$d^4 k a^4 k' = 16 d^4 p d^4 q$$

and get for (11),

$$\begin{aligned} h_{\text{self}} &= \frac{-2f^2}{(2\pi)^3} \int d^4 p d^4 q \left\{ \frac{\delta(q_\mu^2 + p_\mu^2 + 2p_\mu q_\mu + \kappa^2)}{q_\mu^2 + p_\mu^2 - 2p_\mu q_\mu + \kappa^2} \right. \\ &+ \frac{\delta(q_\mu^2 + p_\mu^2 - 2p_\mu q_\mu + \kappa^2)}{q_\mu^2 + p_\mu^2 + 2p_\mu q_\mu + \kappa^2} \left. \right\} \{ \varphi(x), \varphi(2q) \} e^{i2q_\mu x_\mu} \delta(4q_\mu^2 + m^2) \\ &= \frac{f^2}{(2\pi)} \int \frac{d^4 p d^4 q}{2p_\mu q_\mu} \{ \delta(q_\mu^2 + p_\mu^2 + 2p_\mu q_\mu + \kappa^2) \\ &- \delta(q_\mu^2 + p_\mu^2 - 2p_\mu q_\mu + \kappa^2) \} \{ \varphi(x), \varphi(2q) \} e^{i2q_\mu x_\mu} \delta(4q_\mu^2 + m^2). \end{aligned} \quad (13)$$

With the aid of the identity (Schwinger 1949 a)

$$\frac{1}{B} (\delta(A+B) - \delta(A-B)) = \int_{-1}^1 du \delta'(A+Bu), \quad (14)$$

(13) becomes

$$\begin{aligned} h_{\text{self}} &= \frac{f^2}{(2\pi)} \int d^4 p d^4 q \int_{-1}^1 du \delta'(q^2 + p^2 + \kappa^2 \\ &+ 2p_\mu q_\mu u) \{ \varphi(x), \varphi(2q) \} e^{i2q_\mu x_\mu} \delta(4q_\mu^2 + m^2). \end{aligned} \quad (15)$$

Introduce:

$$\xi_\mu = p_\mu + u q_\mu \quad (16)$$

If we also replace q_μ by $\frac{1}{2}q_\mu$ this substitution gives for (15):

$$\begin{aligned} h_{\text{self}} &= \frac{f^2}{16(2\pi)^3} \int d^4 \xi d^4 q \int_{-1}^1 du \delta'[\xi^2 + \frac{1}{4}q^2(1-u^2) \\ &+ \kappa^2] \{ \varphi(x), \varphi(q) \} e^{iq_\mu x_\mu} \delta(q^2 + m^2). \end{aligned} \quad (17)$$

Thus, we may write

$$h_{\text{self}} = \delta_1 m^2 \varphi^2(x) \quad (18)$$

with

$$\delta_1 m^2 = \frac{f^2}{8(2\pi)^3} \int d^4 \xi \int_{-1}^1 du \delta'[\xi^2 - \frac{m^2}{4}(1-u^2) + \kappa^2]. \quad (18')$$

Denoting

$$\kappa^2 - \frac{1}{4} m^2 (1 - u^2) = A \quad (19)$$

we may write

$$\delta'(\xi^2 + A) = \frac{i}{(2\pi)} \int_{-\infty}^{+\infty} dw \, w \, e^{i(\xi^2 + A)w}, \quad (20)$$

whence

$$d_1 m^2 = \frac{if^2}{8(2\pi)^4} \int d^4 \xi \int_{-1}^1 du \int_{-\infty}^{\infty} dw \cdot w \cdot e^{i(\xi^2 + A)w} \quad (21)$$

With the aid of the formula

$$\int d^4 \xi \, e^{i\xi^2 w} = \frac{i\pi^2}{w^2} \varepsilon(w) \quad (22)$$

with

$$\varepsilon(w) = \begin{cases} +1 & \text{for } w > 0 \\ -1 & \text{,, } w < 0 \end{cases} \quad (23)$$

and integrating by parts with respect to u we get

$$\begin{aligned} \delta_1 m^2 &= \frac{-f^2}{32(2\pi)^2} \int_{-1}^1 du \int_{-\infty}^{\infty} dw \frac{\varepsilon(w)}{w} e^{iAw} \\ &= -\frac{f^2}{16(2\pi)^2} \int_{-1}^1 du \int_{-\infty}^{\infty} \frac{dw}{w} \cos Aw \\ &= \frac{-f^2}{8(2\pi)^2} \int_0^{\infty} dw \left\{ \frac{\cos w}{w} + \frac{m^2}{4} \int_{-1}^1 du \, u^2 \sin \left[\kappa^2 - \frac{m^2}{4} (1 - u^2) \right] w \right\} \\ &= \frac{-f^2}{8(2\pi)^2} \left\{ \int_0^{\infty} dw \frac{\cos w}{w} + \int_{-1}^1 du \frac{u^2}{u^2 - 1 + 4\kappa^2/m^2} \right\}. \end{aligned} \quad (24)$$

The first integral is logarithmically divergent at the lower limit. The second integral is convergent if

$$1 - \frac{4\kappa^2}{m^2} \leq 0$$

and convergent in the sense of Cauchy if

$$0 < 1 - \frac{4\kappa^2}{m^2} < 1.$$

(b) *Coupling with a spinor field.* To cancel the divergence in (24) we have at our disposal the interaction of the C -meson with a spinor field (spin $1/2$). The interaction Hamiltonian adopted for our purposes is³

$$h = g v \varphi \quad (25)$$

where v is composed of Dirac spinors ψ_α and $\bar{\psi}_\alpha$ (not to be confused with the charged meson field φ, φ^*) in the following way

$$v = \bar{\psi}_\alpha \psi_\alpha \equiv \bar{\psi} \psi. \quad (25')$$

We transform away the first order terms by means of (5) with

$$\frac{\delta S[\sigma]}{\delta \sigma(x)} = g v \varphi$$

and obtain an expression of the same shape as (6) with ϱ replaced by v and f by g . The self energy of the C -meson due to the interaction with a spinor field is the „one C -meson part“ of this expression (analogue to (7)):

$$h_{\text{self}} = -\frac{i g^2}{8} \int d^4 x' \varepsilon[\sigma \sigma'] \langle [v, v'] \rangle_0 \{\varphi, \varphi'\}. \quad (26)$$

Using the well known commutation rules and the vacuum expectation values for a spinor field (Schwinger 1948, 1949) we easily get

$$h_{\text{self}} = g^2 \int d^4 x \left(\frac{\partial \bar{\Delta}}{\partial x_\nu} \frac{\partial \Delta^{(1)}}{\partial x_\nu} - \kappa_s^2 \bar{\Delta} \Delta^{(1)} \right) \{\varphi, \varphi'\}, \quad (27)$$

where κ_s is the mass constant of a spinor field, $\Delta^{(1)}$ and Δ refer to the spinor field. The calculation of (27) may be carried out by exactly the same methods and yields

$$h_{\text{self}} = \delta_2 m^2 \varphi^2(x) \quad (28)$$

³ The coupling

$$i g' j_\nu \frac{\partial \varphi}{\partial x_\nu} - \frac{1}{2} g'^2 j_\nu N_\nu j_\mu N_\mu$$

leads to a remarkable result i. e. to a finite value for the self energy:

$$h_{\text{self}} = -\frac{g'^2 m^2}{2(2\pi)^2} \left(\kappa_s^2 - \frac{m^2}{6} \right) \varphi^2$$

thus, the coupling with g' is of no use for the cancellation. As our aim has been to find the most simple system of fields we have put $g' = 0$ and considered only the coupling (25).

with

$$\delta_2 m^2 = \frac{g^2}{2(2\pi)^2} \left\{ 3 \left(\kappa_s^2 - \frac{m^2}{6} \right) \int_0^\infty dw \frac{\cos w}{w} \right. \\ \left. + \frac{m^2}{4} \int_{-1}^1 du \, u^2 \frac{u^2 - 3 + 12\kappa_s^2/m^2}{u^2 - 1 + 4\kappa_s^2/m^2} + 2 \left(\kappa_s^2 - \frac{m^2}{6} \right) \right\} \quad (28')$$

By comparing (24) with (28') we see that the divergences cancel each other if

$$f^2 = 2g^2(6\kappa_s^2 - m^2) \quad (29)$$

which may be satisfied by a suitable choice of the coupling constants f and g provided

$$6\kappa_s^2 > m^2 \quad (30)$$

We have, therefore, to introduce spinors and C -mesons which satisfy (29) and (30). For a detailed discussion of this point see Section V.

II. Self mass of a charged pseudoscalar meson. (a) *Coupling with a C -meson.* In order to compute the self-energy term for the charged meson we have to take „one (charged) meson part“ of (6') Section I. With the aid of (8) we easily get

$$\{e, e'\}_1 = (\psi^* \psi + \psi^{*\prime} \psi') \Delta_x^{(1)}(0) + (\psi^{*\prime} \psi + \psi^* \psi') \Delta_x(x - x'). \quad (1)$$

Thus, the whole self-energy operator may be written in the form:

$$h_{\text{self}} = h_{\text{self}}^{\text{I}} + h_{\text{self}}^{\text{II}} \quad (2)$$

with

$$h_{\text{self}}^{\text{I}} = -\frac{f^2}{4} \Delta_x^{(1)}(0) \int d^4 x' \bar{\Delta}_m(\psi^* \psi + \psi^{*\prime} \psi') \quad (2')$$

$$h_{\text{self}}^{\text{II}} = -\frac{f^2}{4} \int d^4 x' (\Delta_m^{(1)} \bar{\Delta} + \bar{\Delta}_m \Delta_x^{(1)}) (\psi^{*\prime} \psi + \psi^* \psi') \quad (2'')$$

The arguments of the Δ -functions under the integrals are $x_\mu - x'_\mu$. We notice the existence of a term with $\Delta_x^{(1)}(0)$. This term has been obtained by taking the „one particle part“ of $\{e, e'\}$ where, among others, exist terms of the type

$$\langle \psi^* \psi \rangle_0 \psi^* \psi'.$$

In a charge symmetric theory similar terms generally cancel. Here, on the contrary, they remain since the scalar-scalar coupling is not charge symmetric.

The first term in (2') may be immediately put into the form of a mass renormalization factor:

$$-\frac{f^2}{4} \Delta_{\pi}^{(1)}(0) \psi^* \psi \int d^4 x' \bar{\Delta}_m = -\frac{f^2}{4m^2} \Delta_{\pi}^{(1)}(0) \psi^* \psi. \quad (3)$$

The second term in (2) is not of such simple form. By Fourier analysing the functions ψ' , $\psi^{*'}$ and $\bar{\Delta}_m$ we have

$$-\frac{f^2}{4} \Delta_{\pi}^{(1)}(0) \int d^4 k \int d^4 k' \psi^*(k') \psi(k) \delta(k^2 + \kappa^2) \delta(k'^2 + \kappa^2) \frac{e^{i(k_{\mu} - k'_{\mu})x_{\mu}}}{(k_{\mu} - k'_{\mu})^2 + m^2}. \quad (4)$$

From this last expression we see, however, that its diagonal elements are identical with those of

$$-\frac{f^2}{4} \Delta_{\pi}^{(1)}(0) \int d^4 k \int d^4 k' \psi^*(k') \psi(k) \delta(k' + \kappa^2) \delta(k'^2 + \kappa^2) \frac{e^{i(k_{\mu} - k'_{\mu})x_{\mu}}}{m^2}$$

which again is identical with (3). Thus

$$h_{\text{self}}^1 = \delta_1 \kappa^2 \psi^* \psi \quad (4')$$

with

$$\delta_1 \kappa^2 = -\frac{f^2}{2m^2} \Delta_{\pi}^{(1)}(0) \quad (5)$$

where

$$\Delta_{\pi}^{(1)}(0) = \frac{1}{(2\pi)^3} \int d^4 k \delta(k_{\mu}^2 + \kappa^2) \quad (6)$$

By integrating (6) over k_0 first we would get a quadratically divergent integral:

$$\int_0^{\infty} \frac{k^2 dk}{\sqrt{k^2 + \kappa^2}}$$

but if we represent the δ -function as a Fourier integral:

$$\delta(k_{\mu}^2 + \kappa^2) = \frac{1}{(2\pi)} \int_{-\infty}^{+\infty} dw e^{i(k_{\mu}^2 + \kappa^2)w}, \quad (7)$$

change the order of integrations and use (22) from the foregoing section then we get

$$\Delta_{\pi}^{(1)}(0) = \frac{i}{16\pi^2} \int_{-\infty}^{+\infty} \frac{dw}{w^2} \varepsilon(w) e^{i\kappa^2 w} \quad (8)$$

or

$$\Delta_*^{(1)}(0) = \frac{-\kappa^2}{16\pi^2} \left(2 + \int_{-\infty}^{+\infty} \frac{dw}{w} \varepsilon(w) e^{i\kappa^2 w} \right). \quad (9)$$

This is a logarithmically divergent integral over an invariant parameter w . We adopt this last alternative, constituting one of the prescriptions for the evaluation of non-well-defined expressions in quantum field theory.

From (5) and (9) we have:

$$\delta_1 \kappa^2 = \frac{f^2}{16\pi^2} \frac{\kappa^2}{m^2} \left(\int_0^0 dw \frac{\cos w}{w} + 1 \right). \quad (10)$$

Next we evaluate $h_{\text{self}}^{\text{II}}$ from (2''). Using Fourier representations of $\Delta^{(1)}$, $\bar{\Delta}$, ψ and ψ^* we get

$$h_{\text{self}}^{\text{II}} = \frac{-f^2}{4(2\pi)^3} \int d^4 k d^4 k' \left(\frac{\delta[(k_\mu + k'_\mu)^2 + m^2]}{k_\mu^2 + \kappa^2} + \frac{\delta[k_\mu^2 + \kappa^2]}{(k_\mu + k'_\mu)^2 + m^2} \right) \times \delta(k_\mu'^2 + \kappa^2) \psi^*(k') \psi(x) e^{-i k'_\mu x_\mu} + \text{compl. conj.} \quad (11)$$

With the aid of variable transformations similar to those in Section I, we get

$$h_{\text{self}}^{\text{II}} = \delta_2 \kappa^2 \psi^* \psi \quad (12)$$

with

$$\delta_2 \kappa^2 = \frac{-f^2}{16\pi^2} \left(\int_0^\infty dw \frac{\cos w}{w} + \int_0^2 dv \frac{v(v - m^2/\kappa^2)}{v^2 - 2v m^2/\kappa^2 + 4m^2/\kappa^2} \right). \quad (12')$$

(b) *Coupling with the electromagnetic field.* The Schrödinger equation for the pseudoscalar (or scalar) charged meson field coupled with the electromagnetic field is (3) Section I with

$$h' = N_\mu I_{\mu\nu} \dot{N}_\nu, \quad (13)$$

where

$$I_{\mu\nu} = \delta_{\mu\nu} (S_\lambda A_\lambda - e^2 \psi^* \psi A_\lambda A_\lambda) + e^2 \psi^* \psi A_\mu A_\nu, \quad (13')$$

where S_λ is used in short for

$$S_\mu = ie \left(\frac{\partial \psi^*}{\partial x_\mu} \psi - \frac{\partial \psi}{\partial x_\mu} \psi^* \right).$$

If the surface σ is a plane $t = \text{const.}$ then h' becomes the usual interaction part of a Hamiltonian:

$$-S_\lambda A_\lambda + e^2 \psi^* \psi A_i A_i. \quad (13'')$$

We remove again the first order terms with the aid of a unitary transformation and, by taking the „one meson part“, we get

$$h_{\text{self}} = h_{\text{self}}^{\text{I}} + h_{\text{self}}^{\text{II}} \quad (14)$$

where

$$h_{\text{self}}^{\text{I}} = \frac{3}{2} e^2 D^{(1)}(0) \psi^* \psi, \quad (14')$$

$$h_{\text{self}}^{\text{II}} = \frac{e^2}{4} \int d^4 x' \{ D^{(1)} [\bar{\Delta}_\mu (\psi_\mu^{*'} \psi - \psi_\mu^* \psi') + \bar{\Delta} (\kappa^2 \psi^* \psi' - \psi_\mu^{*'} \psi_\mu)] + \bar{D} [\Delta_\mu^{(1)} (\psi_\mu^{*'} \psi - \psi_\mu^* \psi') + \Delta^{(1)} (\kappa^2 \psi^* \psi' - \psi_\mu^{*'} \psi_\mu)] \} + \text{compl. conj.} \quad (14'')$$

where the index μ means the derivatives

$$\psi_\mu = \frac{\partial \psi}{\partial x_\mu}, \quad \psi_\mu' = \frac{\partial \psi'}{\partial x_\mu'}, \quad \Delta_\mu = \Delta_\mu(x - x') = \frac{\partial \Delta(x - x')}{\partial x_\mu}.$$

As the mass constant in $D^{(1)}$ is zero, we have from (8)

$$D^{(1)}(0) = \frac{i}{16\pi^2} \int_{-\infty}^{+\infty} \frac{dw}{w^2} \varepsilon(w) = 0$$

which is identically zero grounds of symmetry⁴. Thus

$$h_{\text{self}}^{\text{I}} = 0. \quad (15)$$

By using the methods displayed in Section I we get from (14'')⁵

$$h_{\text{self}}^{\text{II}} = \delta \kappa^2 \psi^* \psi \quad (16)$$

with

$$\delta \kappa^2 = \frac{e^2}{(2\pi)^3} \int d^4 k (2\kappa^2 - q_\mu k_\mu) \left(\frac{\delta(k^2)}{(q_\mu + k_\mu)^2 + \kappa^2} + \frac{\delta[k_\mu + q_\mu]^2 + \kappa^2}{k_\mu^2} \right) d^4 q. \quad (16')$$

This last integral depends only on $q_\nu^2 = -\kappa^2$ but not on the separate components q_μ . We may introduce invariant parameters u and w as

⁴ It should be noted that an elementary computation yields a quadratically divergent result: $D^{(1)}(0) \sim \int_0^\infty k dk$. This is a point where the rules for computation adopted in this paper obviously interfere.

⁵ Some of the terms obtained directly from (14'') are of the form $C \frac{\partial \psi^*}{\partial x_\mu} \frac{\partial \psi}{\partial x_\mu}$. However, this may be put into the usual form of a mass renormalization term $-\kappa^2 C \psi^* \psi$ by using a method displayed by one of us elsewhere. (Rzewuski, 1950).

usually and get

$$\delta \kappa^2 = \frac{e^2 \kappa^2}{64\pi^2} \int_{-1}^1 du \int_{-\infty}^{\infty} dw \frac{\varepsilon(w)}{w} e^{iAw} (5+u) \quad (17)$$

with

$$A = \frac{\kappa^2}{4} (u-1)^2$$

or, finally (Mc Connell 1949),

$$\delta \kappa^2 = \frac{3}{16\pi^2} e^2 \kappa^2 \left(\int_0^{\infty} dw \frac{\cos w}{w} + \frac{5}{2} \right). \quad (18)$$

By comparing the results (10), (12'), (15) and (18) we see that the divergent parts yield together

$$\frac{1}{16\pi^2} \left(\frac{f^2}{m^2} (m^2 - \kappa^2) - 3 e^2 \kappa^2 \right) \lg \alpha \quad (\alpha \rightarrow 0),$$

whence the condition for compensation is

$$f^2 = 3 e^2 \frac{\kappa^2 m^2}{m^2 - \kappa^2} \quad (19)$$

III. Self mass of fermions. For fermions with spin 1/2 we have already introduced in Section I (25) the interaction with C -mesons. On the other hand we have the interaction with the electromagnetic field discussed by Schwinger² and the possible interaction with charged pseudoscalar mesons. We assume the last one to be zero as has been generally assumed in the case of electrons. This point, however, will be fuller discussed in Section V.

The self energy of fermions due to the interaction with the electromagnetic field is given in Schwinger's (1949 a) formula (3.97) and has the form (in our notation)

$$\delta \kappa_s = \frac{3}{16\pi^2} e^2 \kappa_s \left(\int_0^{\infty} dw \frac{\cos w}{w} + \frac{5}{3} \right). \quad (1)$$

We have to compute only the „one fermion part“ of the Hamiltonian (25) Section I transformed to the second order. This yields

$$h_{\text{self}} = h_{1s} = \bar{\psi} \varphi + \bar{\varphi} \psi \quad (2)$$

with

$$\begin{aligned} \varphi = \frac{g^2}{4} \int d^4 x' \left\{ \gamma_\nu \left[\frac{\partial \Delta^{(1)}}{\partial x_\nu} \bar{\Delta}_m + \frac{\partial \bar{\Delta}}{\partial x_\nu} \Delta_m^{(1)} \right] \right. \\ \left. - \kappa_s [\Delta^{(1)} \bar{\Delta}_m + \bar{\Delta} \Delta_m^{(1)}] \right\} \psi', \end{aligned} \quad (2')$$

where $\bar{\Delta}_m$ and $\Delta_m^{(1)}$ denote the delta functions associated with the C -mesons and $\bar{\Delta}$ and $\Delta^{(1)}$ those associated with the spinor particles as before. After introduction of Fourier transforms we get

$$\delta\kappa = -\frac{3}{8} \frac{g^2 \kappa_s}{(2\pi)^2} \left\{ \int_0^\infty dw \frac{\cos w}{w} + \frac{1}{6} \int_{-1}^1 du \frac{u(6-u)(1-m^2/\kappa_s^2+u)}{1+2m^2/\kappa_s^2+2(1-m^2/\kappa_s^2)u+u^2} \right\}. \quad (3)$$

Comparison of (1) and (3) shows that a finite result is obtained by putting

$$g^2 = 2e^2 \quad (4)$$

which confirms the older results of Pais (1947). We could as well take the coupling constant $g=e$ but introduce two C -meson fields for each spinor field.

IV. Self mass of photons. It has been shown by R. Jost (1949) and one of the present authors that the self mass of photons vanishes identically provided the electromagnetic field is coupled not only with spinors but also with charged pseudoscalar (or scalar) mesons. If we denote the number of spinor fields by n and the number of pseudoscalar charged meson fields by n' then the conditions for compensation are

$$n' = 2n \quad (1)$$

$$\sum_{i=1}^{n'} \kappa_i^2 = 2 \sum_{i=1}^n (\kappa_i^{(s)})^2, \quad (2)$$

where κ_i ($i=1,2,\dots,n'$) mean the masses of meson particles, $\kappa_i^{(s)}$ ($i=1,2,\dots,n$) those of spinor particles.

V. Concluding remarks. The mathematically simplest way to satisfy (1) and (2) of Section IV is to assume a single spinor field (electrons with mass κ_e) and two charged scalar (or pseudoscalar) meson fields with masses

$$\kappa_1 = \kappa_2 = \kappa_e \quad (1)$$

Now, condition (29) of Section I, becomes

$$f^2 = g^2(6\kappa_e^2 - m^2) \quad (2)$$

since there are two charged meson fields. From (4) Section III we get

$$f^2 = 2e^2(6\kappa_e^2 - m^2). \quad (2')$$

Comparing (2') with (19) Section II we find

$$\frac{3\kappa_e^2 m^2}{m^2 - \kappa_e^2} = 2(6\kappa_e^2 - m)^2 \quad (3)$$

together with the inequalities:

$$6\kappa_e^2 > m^2 > \kappa_e^2. \quad (3')$$

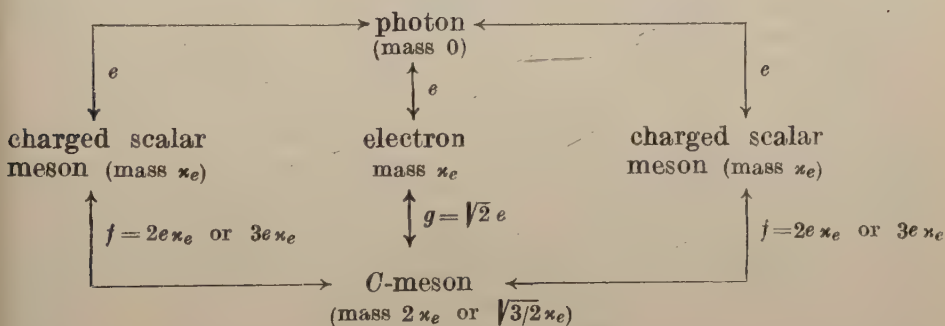
From (3)

$$m^2 = 4\kappa_e^2 \quad \text{or} \quad m^2 = \frac{3}{2}\kappa_e^2 \quad (4)$$

both being compatible with (3'). Finally, from (2') we obtain

$$f = \pm 2e\kappa_e \quad \text{or} \quad f = \pm 3e\kappa_e, \quad (5)$$

thus, our conditions for compensations are compatible and the simplest closed system of mutually compensating fields may be pictured schematically as follows



We notice the lack of interaction between the charged particles and between the neutral ones.

The above system, distinguished by its mathematical simplicity, is difficult to accept from the physical point of view; indeed, all the particles in question possess masses of the order of magnitude of the electron mass and thus do not deserve the name of mesons. But more general solutions exist too. If we introduce (besides the electron) another spinor field with a large mass constant, then we have to introduce four charged scalar or pseudoscalar fields with larger masses κ_i ($i=1, \dots, 4$) to satisfy conditions (1) and (2) of Section IV. The C mesons will then be suitably heavier too.

It should not be forgotten, however, that if these heavy spinor particles were protons then we should also admit the nuclear forces. In order to compensate the divergences due to the nuclear forces we

must look for further suitable fields. As our present knowledge of nuclear interactions is still incomplete we consider the investigation of nuclear compensations as premature and limit ourselves to a completion of quantum electrodynamics.

After the elimination of divergences of the mass renormalization type, the procedure of mass renormalization described by Schwinger (1948, 1949) and Dyson (1949) becomes meaningful.

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THE TORSIONAL OSCILLATOR

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A quantum-mechanical theory of the torsional oscillator is given. In order to obtain the Schrödinger equation in a form suitable for this problem, the classical kinetic energy of the torsional oscillator is expressed in terms of four Euler's symmetrical parameters; the first three of them are taken as independent variables. The resulting Schrödinger equation cannot be solved exactly by separation of variables. This can be done, however, after dropping some terms which are small so long as the amplitudes of the torsional vibrations are small. The equation without these terms is considered as the unperturbed Schrödinger equation and the neglected terms as the small perturbation whose effects have to be calculated by Schrödinger's perturbation theory.

The unperturbed equation must be transformed to normal coordinates if the axes of the ellipsoid of moments of inertia and that of moments of torsion do not coincide. It leads to energy levels and eigenfunctions which approach those of a spatial oscillator if some simplifications are introduced. In the simplest and physically most important case, in which the axes of both ellipsoids coincide, one obtains the eigenvalues and eigenfunctions of the torsional oscillator by replacing masses by principal moments of inertia and displacements by angles of rotation about principal axes of inertia in the eigenvalues and eigenfunctions of a spatial oscillator. By means of perturbation theory, the first approximation is calculated for an oscillator with coinciding principal axes of inertia and those of moments of torsion for the non-degenerate case.

The theory is applicable to the torsional vibrations of molecules in crystals or in rigid solutions. The validity of approximations made is tested by using the experimental results of the investigations of the so-called external Raman effect produced by the torsional vibrations of molecules in molecular crystals. The estimation shows that even the solutions of the unperturbed equation are quite a good approximation: the error of the eigenvalues does not exceed few per cent and that of the eigenfunctions few per cent (for small quantum numbers). The estimate was carried out for the pure crystal of naphthalen, but the result holds also for all the molecules fulfilling a certain general condition.

A formula giving the probability distribution of orientations of the torsional oscillator is also given.

I. Introduction. Many phenomena occurring in solid and liquid media are connected with torsional oscillations. By this term we de-

note a motion consisting of multiply periodic changes of orientation in the neighbourhood of a certain position of equilibrium. Oscillations of this kind are possible when the molecules behave like rigid bodies placed in a field of external forces, i. e. when the forces connecting the atoms within a molecule are considerably larger than those acting between the molecules, yet the latter suffice to keep the molecules near a position of equilibrium. Such conditions are realized in vitreous liquids and in molecular crystals at low temperatures. With the increase of temperature the torsional oscillations pass into rotational motion.

In liquids having a very large coefficient of viscosity, the torsional oscillations of fluorescent molecules must become apparent in a partial depolarization of photoluminescence (Jabłoński 1950). In molecular crystals, both the oscillations and their transition into rotational motion influence the structure and the thermic properties of the crystals. Pauling (1930) and Stern (1931) give quantum considerations, Stern — for diatomic homopolar (covalent) molecules, Pauling — for a particular case of oscillations about a fixed axis. The solution of Schrödinger's equation yields here, as limiting cases, oscillation or rotational motion, the transition from one type of motion to the other being continuous, (in contradistinction to the classical picture).

An effect closely connected with torsional oscillations of molecules is the Raman radiation of small frequency¹ ($\Delta\nu < 150 \text{ cm}^{-1}$), observed in the spectrum of the light dispersed by certain organic molecular crystals (Gross 1935, 1939; Wuks 1937). According to Rousset's theory (1942, 1944 a, 1944 b, 1945, 1947; Kastler 1941, 1944, 1947)² these lines may be attributed to harmonic torsional oscillations of molecules about three axes (being in the simplest case the principal axes of inertia). The starting point of Rousset's theory is the motion of a single molecule (which is regarded as a rigid body), solved in a classical way to a first approximation (for small amplitudes); further considerations are concerned with the theory of the effect in the crystal net, and involve a comparison with existing experimental evidence.

The calculations given below aim at extending the quantum considerations of Pauling and Stern to molecules possessing 3 dif-

¹ This is the so-called „external“ Raman radiation, vanishing at the melting point, which fact bears witness to its association with the crystal structure.

² Later publications accepting the same hypothesis are of Nedungadi (1941 1943), Gross (1945) and Wuks (1915).

ferent principal moments of inertia. They have been carried out on the assumption that the amplitudes are small thus neglecting the problem of the transition from oscillation to rotational motion (in quantum theory this means a limitation to not very high energy levels).

II. Classical expression for the energy of the torsional oscillator. A classical model serving as basis for further considerations is the „asymmetric top“, executing torsional oscillations (according to the definition given in Chapter I) of small amplitude about its centre of mass³ in an external time-independent field of forces⁴. The field of external forces is expressed by the ellipsoid of directing momenta.

Two coordinates systems, with a common origin are introduced: x_0, y_0, z_0 fixed in space, and x, y, z fixed in the body and moving with it; in the equilibrium position the axes of both systems coincide with one another and with the directions of the principal axes of inertia of the body. As variables determining the momentary position of xyz with respect to $x_0y_0z_0$ the symmetric Euler parameters⁵ have been introduced (Whittaker 1944, page 8)

$$\begin{aligned}\xi_1 &= \cos \kappa_1 \sin \frac{\varepsilon}{2} \\ \xi_2 &= \cos \kappa_2 \sin \frac{\varepsilon}{2} \\ \xi_3 &= \cos \kappa_3 \sin \frac{\varepsilon}{2} \\ \xi_4 &= \cos \frac{\varepsilon}{2}\end{aligned}\tag{1}$$

k_1, k_2, k_3 are the angles between the fixed axes and the axis of the rotation which brings the movable set of axes from the original position

³ Neglecting the influence of the simultaneous motion of the centre of mass.

⁴ Both assumptions, that of the immobility of the centre of mass and that of the invariability of the forces, though not strictly corresponding to real physical conditions are yet justified, at least as far as crystal media are concerned (Margenau 1943, pages 19 and 35).

⁵ The application of Euler's angles ϑ, ψ, φ would limit our considerations to the zero-order approximation, since they play the part of „components“ of a small „vector of rotation“ (Rousset 1945, p. 13; 1947, p. 22).

to the given momentary position (l); ε is the angle of rotation about this axis (Fig. 1). The parameters $\xi_1 \dots \xi_4$ satisfy the relation

$$\sum_{i=1}^4 \xi_i^2 = 0. \quad (2)$$

For small amplitudes ($\varepsilon \ll 1$) we shall have

$$|\xi_1| \ll 1, \quad |\xi_2| \ll 1, \quad |\xi_3| \ll 1 \quad (3)$$

$$\xi_4 = +\sqrt{1 - \xi_1^2 - \xi_2^2 - \xi_3^2} \approx 1 - \frac{1}{2}(\xi_1^2 + \xi_2^2 + \xi_3^2) + \dots \quad (4)$$

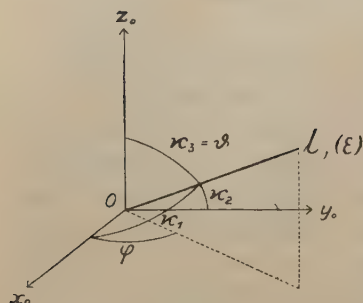


Fig. 1.

Expressing kinetic and potential energies in variables ξ_1, ξ_2, ξ_3 we can develop them into a power-series with respect to ξ_1, ξ_2, ξ_3 . In the calculations here carried out, terms to the second degree inclusively have been taken into account. Limiting the calculations to the first approximation, ξ_1, ξ_2, ξ_3 will have the significance of double „components of the vector of rotation“. This is seen immediately when $\sin \frac{\varepsilon}{2}$ is developed in formulá (1).

The kinetic energy of the asymmetric top is given by

$$T_{kl} = \frac{1}{2} \sum_{i=1}^3 B_i \omega_i^2, \quad (5)$$

where B_i 's denote the principal moments of inertia, ω_i 's — the components of the angular velocity in the xyz -coordinate system. Expressing ω_i in terms of ξ_i by means of the formulae (Whittaker 1944, page 16)

$$\begin{aligned} \omega_1 &= 2(\xi_4 \dot{\xi}_1 + \xi_3 \dot{\xi}_2 - \xi_2 \dot{\xi}_3 - \xi_1 \dot{\xi}_4) \\ \omega_2 &= 2(-\xi_3 \dot{\xi}_1 + \xi_4 \dot{\xi}_2 + \xi_1 \dot{\xi}_3 - \xi_2 \dot{\xi}_4) \\ \omega_3 &= 2(\xi_2 \dot{\xi}_1 - \xi_1 \dot{\xi}_2 + \xi_4 \dot{\xi}_3 - \xi_3 \dot{\xi}_4) \end{aligned} \quad (6)$$

and taking into account relation (4), equation (5) takes the form

$$\begin{aligned} T = 2 \sum_{1,2,3} \{ [B_1(1 + \xi_1^2 - \xi_2^2 - \xi_3^2) + B_2 \xi_3^2 + B_3 \xi_2^2] \dot{\xi}_1^2 \\ + 2[(B_1 + B_2 - B_3) \xi_1 \xi_2 + (B_1 - B_2) \xi_3] \dot{\xi}_1 \dot{\xi}_2 \}. \end{aligned} \quad (7)$$

Here $\sum_{1,2,3}$ denotes the sum resulting from a cyclic rearrangement of the indices 1, 2, 3.

The development of the potential energy as a function of ξ_1, ξ_2, ξ_3 in a series in the neighbourhood of the equilibrium position ($\xi_1 = \xi_2 = \xi_3 = 0$) yields

$$U = U_0 + \sum_{i=1}^3 \xi_i \left(\frac{\partial U}{\partial \xi_i} \right)_0 + \frac{1}{2} \sum_{i,j=1}^3 \xi_i \xi_j \left(\frac{\partial^2 U}{\partial \xi_i \partial \xi_j} \right)_0 + \dots = 2 \sum_{i,j=1}^3 u_{ij} \xi_i \xi_j \quad (8)$$

where

$$4u_{ij} = \left(\frac{\partial^2 U}{\partial \xi_i \partial \xi_j} \right)_0 \quad (8')$$

(it always may be assumed, without limitation of the generality of the considerations, that $U_0 = 0$, and in the equilibrium position $\left(\frac{\partial U}{\partial \xi_i} \right)_0 = 0$).

The formulae (7), (8) express the energy of the torsional oscillator

$$E = T + U \quad (9)$$

III. Schrödinger's equation for the torsional oscillator.

The quantum operator of the kinetic energy may be obtained on the basis of analogy to cartesian coordinates (19) page 190, 350, by calculating the Laplacian

$$\nabla^2 \psi = \frac{1}{\sqrt{g}} \sum_{i,k=1}^3 \frac{\partial}{\partial \xi_i} \left(\sqrt{g} g^{ik} \frac{\partial}{\partial \xi_k} \psi \right) \quad (10)$$

in coordinates ξ_i , in which the arc element is expressed by the formula

$$ds^2 = 2T_{kl} dt^2 = \sum_{k=1}^3 g_{lk} d\xi_l d\xi_k \quad (11)$$

The symmetric matrix g_{lk} is obtained immediately from the formula (7); g denotes the determinant of this matrix, and g^{lk} — an element of the inverse matrix. The volume element, required for further considerations, is given by the formula

$$d\tau = \sqrt{g} d\xi_1 d\xi_2 d\xi_3 \quad (12)$$

On carrying out the calculations, one obtains for the kinetic energy operator the expression

$$\begin{aligned}
T = & -\frac{\hbar^2}{2} \nabla^2 = -\frac{\hbar^2}{8} \sum_{1,2,3} \left\{ \frac{1}{B_1} \frac{\partial^2}{\partial \xi_1^2} - 8\gamma \frac{\partial}{\partial \xi_1} \right. \\
& + 2 \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \xi_1 \frac{\partial^2}{\partial \xi_2 \partial \xi_3} + \left[-\frac{1}{B_1} \xi_1^2 + \left(\frac{1}{B_3} - \frac{1}{B_1} \right) \xi_2^2 - \left(\frac{1}{B_2} - \frac{1}{B_1} \right) \xi_3^2 \right] \frac{\partial^2}{\partial \xi_1^2} \\
& \left. - \frac{2}{B_1} \xi_2 \xi_3 \frac{\partial^2}{\partial \xi_2 \partial \xi_3} - \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \xi_2 \xi_3 \frac{\partial}{\partial \xi_1} \right\} \\
8\gamma = & \frac{1}{B_1} + \frac{1}{B_2} + \frac{1}{B_3}
\end{aligned} \quad (13)$$

$$8\gamma = \frac{1}{B_1} + \frac{1}{B_2} + \frac{1}{B_3} \quad (13')$$

and hence Schrödinger's equation

$$T\psi + 2 \sum_{i,j=1}^3 u_{ij} \xi_i \xi_j = E\psi. \quad (14)$$

As it is seen, the equation cannot be solved exactly, yet we can get an approximate solution, neglecting in $T\psi$ the small terms which will constitute the „perturbation“. The estimate is founded on assumption (3). To the unperturbed equation will belong the terms $\frac{1}{B_i} \frac{\partial^2 \psi}{\partial \xi_i^2}$ and $8\gamma \frac{\partial \psi}{\partial \xi_i}$. These latter may be included, without spoiling the separability of the equation. Besides, as appears from further calculations, they yield only a small correction, of the same order as that of the other terms, included in the perturbation.

IV. Transformation to the normal coordinates. The unperturbed Schrödinger equation is of the form

$$-\frac{\hbar^2}{8} \sum_{(i)} \left(\frac{1}{B_i} \frac{\partial^2 \psi}{\partial \xi_i^2} - 8\gamma \xi_i \frac{\partial \psi}{\partial \xi_i} \right) + 2 \sum_{(i,j)} (u_{ij} \xi_i \xi_j) \psi = E\psi \quad i, j = 1, 2, 3, \quad (15)$$

(γ given by the formula (13')). It can be integrated by separation of variables, if the potential energy does not involve the mixed terms

$$u_{ij} = 0, \quad i \neq j \quad (16)$$

In the general case, these terms can be removed by transformation to normal coordinates, i. e. by simultaneous reduction to their canonical form of the kinetic and potential energies, which to a zero approximation are homogeneous quadratic forms (the kinetic energy is positive definite). (Courant and Hilbert 1937, page 30; Herzberg 1945, page 61)

$$\eta_i = 2\sqrt{B_i} \zeta_i \quad i=1,2,3 \quad (17)$$

$$T = \frac{1}{2} \sum_{(i)} \eta_i^2 \quad (17')$$

$$U = \frac{1}{2} \sum_{(i,j)} \frac{u_{ij}}{\sqrt{B_i B_j}} \eta_i \eta_j \quad (17'')$$

$$\zeta_i = \sum_{(j)} a_{ij} \eta_j \quad i, j=1,2,3, \quad (18)$$

$$\sum_{(i)} a_{ij} a_{ik} = \delta_{jk}; \quad \sum_{(i)} a_{ji} a_{ki} = \delta_{jk} \quad (18')$$

$$T = \frac{1}{2} \sum_{(i)} \zeta_i^2 \quad (18'')$$

$$U = \frac{1}{2} \sum_{(i)} \lambda_i \zeta_i^2 \quad (18''')$$

The coefficients λ_i are the roots of the secular equation

$$\left| \frac{u_{ij}}{\sqrt{B_i B_j}} - \delta_{ij} \lambda \right| = 0 \quad i, j=1,2,3, \quad (19)$$

which, at the same time, is the condition of solvability of a set of linear equations

$$\sum_{(j)} \left(\frac{u_{ij}}{\sqrt{B_i B_j}} - \delta_{ij} \lambda_k \right) a_{ij} = 0 \quad i, k=1,2,3, \quad (20)$$

yielding together with (18') the coefficients of transformation (18).

Carrying out successively the transformations (17), (18) we obtain⁶

$$-\frac{\hbar^2}{2} \sum_{(i)} \left(\frac{\partial^2 \psi}{\partial \eta_i^2} - 2\gamma \eta_i \frac{\partial \psi}{\partial \eta_i} \right) + \frac{1}{2} \sum_{(i,j)} \left(\frac{u_{ij}}{\sqrt{B_i B_j}} \eta_i \eta_j \right) \psi = E\psi \quad (21)$$

$$T = -\frac{\hbar^2}{2} \sum_{(i)} \left\{ \sum_{(k,l)} \frac{\partial^2 \psi}{\partial \zeta_k \partial \zeta_l} a_{ki} a_{li} - 2\gamma \sum_{(j)} a_{ji} \zeta_j \sum_{(k)} \frac{\partial \psi}{\partial \zeta_k} a_{ki} \right\} \quad (22)$$

$$= -\frac{\hbar^2}{4} \sum_{(k)} \left(\frac{\partial^2 \psi}{\partial \zeta_k^2} - 2\gamma \zeta_k \frac{\partial \psi}{\partial \zeta_k} \right)$$

$$-\frac{\hbar^2}{2} \sum_{(k)} \left(\frac{\partial^2 \psi}{\partial \zeta_k^2} - 2\gamma \zeta_k \frac{\partial \psi}{\partial \zeta_k} \right) + \frac{1}{2} \sum_{(k)} \lambda_k \zeta_k^2 \psi = E\psi. \quad (23)$$

⁶ It seems more convenient to start straightforwardly with the quantum expression (15). The terms containing the first derivatives are also invariants of the two transformations.

As is seen from formulae (21), (23), Schrödinger's equation in the variables ζ_i has in the general case the same form as in the variables η_i , assuming (16). Only $\frac{u_{ii}}{B_i}$'s are replaced by λ_i 's. Therefore it suffices to solve the equation for case (16), and the result can easily be generalized for arbitrary u_{ij} 's.

V. Solution of the unperturbed equation. Assuming (16), equation (21) can be solved by separation of variables

$$\psi = \psi_1(\eta_1) \cdot \psi_2(\eta_2) \cdot \psi_3(\eta_3) \quad (24)$$

$$\psi_i'' - 2\gamma \psi_i' + \frac{2}{\hbar} \left(E_i - \frac{1}{2} \frac{u_{ii}}{B_i} \eta_i^2 \right) \psi_i = 0 \quad i=1,2,3, \quad (25)$$

$$E_1 + E_2 + E_3 = E. \quad (26)$$

The first derivative in formula (25) is removed by the substitution (Mott and Massey 1933)

$$\psi_i = u_i(\eta_i) \cdot e^{\frac{1}{2}\gamma \eta_i^2} \quad (27)$$

(γ expressed by (13')), and we obtain

$$u_i'' + u_i \left[\left(\gamma + \frac{2}{\hbar} E_i \right) - \left(\gamma^2 + \frac{1}{\hbar^2} \frac{u_{ii}}{B_i} \right) \eta_i^2 \right] = 0 \quad (27')$$

or

$$u_i'' + u_i(e_i - a_i \eta_i^2) = 0 \quad (28)$$

when denoting

$$\gamma = \frac{2}{\hbar} E_i = e_i; \quad \gamma^2 + \frac{1}{\hbar^2} \frac{u_{ii}}{B_i} = a_i^2. \quad (29)$$

This is the equation of the harmonic oscillator, the solution of which are Hermit's orthogonal functions

$$u_i = N_{n_i} e^{-\frac{1}{2} a_i \eta_i^2} \cdot H_{n_i}(\sqrt{a_i} \eta_i). \quad (30)$$

Considering the geometrical significance of the variables η_i it follows that

$$|\eta_i| \leq 2\sqrt{B_i}. \quad (31)$$

Yet in approximate considerations the interval $-2\sqrt{B_i}; +2\sqrt{B_i}$ can be replaced by an infinite one, provided the exponential function decreases sufficiently rapidly, i. e. when (Assumption I)

$$a_i B_i \gg 1. \quad (32)$$

The eigenfunctions of the unperturbed equation will be of the form

$$\psi_i = N'_{n_i} e^{-\frac{1}{2}(\alpha_i - \gamma)\eta_i^2} \cdot H_{n_i}(\sqrt{\alpha_i} \eta_i) \quad (33)$$

$$\psi_{n_1 n_2 n_3} = N'_{n_1 n_2 n_3} \cdot e^{-\frac{1}{2}[(\alpha_1 - \gamma)\eta_1^2 + (\alpha_2 - \gamma)\eta_2^2 + (\alpha_3 - \gamma)\eta_3^2]} \cdot H_{n_1} \cdot H_{n_2} \cdot H_{n_3} \quad (34)$$

thus will differ from the Hermite's orthogonal functions by the factor⁷

$$e^{\frac{1}{2}\gamma(\eta_1^2 + \eta_2^2 + \eta_3^2)}. \quad (35)$$

This factor may be neglected in an approximation (Assumption II), if

$$\alpha_i \gg \gamma. \quad (36)$$

It can be proved that the conditions (32) and (36) are equivalent to each other, if only B_1, B_2, B_3 are quantities of the same order⁸.

On the simplifying assumption (II), the eigenfunctions of the unperturbed equation assume the form

$$\psi_{n_1 n_2 n_3} = N_{n_1 n_2 n_3} e^{-\frac{1}{2}(\alpha_1 \eta_1^2 + \alpha_2 \eta_2^2 + \alpha_3 \eta_3^2)} \cdot H_{n_1}(\sqrt{\alpha_1} \eta_1) \cdot H_{n_2}(\sqrt{\alpha_2} \eta_2) \cdot H_{n_3}(\sqrt{\alpha_3} \eta_3) \quad (37)$$

$$N_{n_1 n_2 n_3} = \left\{ \frac{\sqrt{\alpha_1 \alpha_2 \alpha_3}}{(\pi)^{3/2}} \frac{1}{2^{n_1 + n_2 + n_3} n_1! n_2! n_3!} \right\}^{\frac{1}{2}} \quad (37')$$

or (expressed in the original variables ξ_i)

$$\psi_{n_1 n_2 n_3} = N_{n_1 n_2 n_3} e^{-\frac{1}{2}(\beta_1 \xi_1^2 + \beta_2 \xi_2^2 + \beta_3 \xi_3^2)} \cdot H_{n_1}(\sqrt{\beta_1} \xi_1) \cdot H_{n_2}(\sqrt{\beta_2} \xi_2) \cdot H_{n_3}(\sqrt{\beta_3} \xi_3) \quad (38)$$

$$N_{n_1 n_2 n_3} = \left\{ \frac{\sqrt{\beta_1 \beta_2 \beta_3}}{8 \sqrt{B_1 B_2 B_3} (\pi)^{3/2} 2^{n_1 + n_2 + n_3} n_1! n_2! n_3!} \right\}^{\frac{1}{2}} \quad (38')$$

$$\beta_i = \frac{4}{\hbar} \sqrt{B_i u_{ii}} = \frac{4}{\hbar} B_i \omega_i = 4 \alpha_i B_i. \quad (39)$$

With the same approximation we can omit (because of condition (36)) the terms of higher order, appearing in the volume element

$$d\tau = 8 \sqrt{B_1 B_2 B_3} \left(1 + \sum_{(i)} \xi_i^2 \right) d\xi_1 d\xi_2 d\xi_3 = \left(1 + \frac{1}{8} \sum_{(i)} \frac{\eta_i^2}{B_i} \right) d\eta_1 d\eta_2 d\eta_3 \quad (40)$$

⁷ The functions (34) vanish at ∞ , since according to (29) we always have

$$\alpha_i > \gamma.$$

⁸ (a) if $\gamma \ll \alpha_i$, then $\frac{1}{8B_i} \ll \alpha_i$, $8\alpha_i B_i \gg 1$, thus also $\alpha_i B_i \gg 1$.

(b) if $\alpha_i B_i \gg 1$, i. e. $\frac{1}{B_i} \ll \alpha_i$ and $\gamma = \frac{1}{8} \left(\frac{1}{B_1} + \frac{1}{B_2} + \frac{1}{B_3} \right) \approx \frac{3}{8} \frac{1}{B_i}$, then $\frac{3}{8} \frac{1}{B_i} \ll \alpha_i$

and thus $\gamma \ll \alpha_i$.

$$d\tau = d\eta_1 d\eta_2 d\eta_3 \quad (40')$$

(Assumption III) ⁹.

The eigenvalues of equation (28) are given by the formula

$$e_i = (2n_i + 1) a_i \quad (41)$$

whence, taking into account (29), we get

$$E_i = \hbar^2 \left(n_i + \frac{1}{2} \right) \sqrt{\frac{1}{\hbar^2} \frac{u_{ii}}{B_i} + \gamma^2} - \frac{\hbar^2}{2} \gamma. \quad (42)$$

Expression (42) is simplified, if, taking into account condition (36) we adopt (Assumption IV)

$$a_i^2 = \frac{1}{\hbar^2} \frac{u_{ii}}{B_i}, \quad a_i = \frac{1}{\hbar} \sqrt{\frac{u_{ii}}{B_i}}, \quad (a_i > 0) \quad (43)$$

namely

$$E_i = \hbar \left(n_i + \frac{1}{2} \right) \sqrt{\frac{u_{ii}}{B_i} - \frac{\hbar^2}{2} \gamma} \quad (44)$$

$$E = E_1 + E_2 + E_3 = E^0 + E'' \quad (45)$$

$$E^0 = \hbar \left\{ \left(n_1 + \frac{1}{2} \right) \sqrt{\frac{u_{11}}{B_1}} + \left(n_2 + \frac{1}{2} \right) \sqrt{\frac{u_{22}}{B_2}} + \left(n_3 + \frac{1}{2} \right) \sqrt{\frac{u_{33}}{B_3}} \right\} \quad (46)$$

$$E'' = -\frac{3}{16} \hbar^2 \left(\frac{1}{B_1} + \frac{1}{B_2} + \frac{1}{B_3} \right) \quad (46')$$

$$\sqrt{\frac{u_{ii}}{B_i}} = \omega_i = 2\pi \nu_i. \quad (47)$$

Besides, from relation (36) it follows that $E'' \ll E^0$ so that E'' may be neglected to a zero approximation. The eigenvalues of the unperturbed equation are then given by formula (46).

In conformity with the remark at the end of the preceding chapter, the above considerations, referring to case (16) may be generalized for arbitrary u_{ij} 's. The eigenvalues will then be of the form

$$E^0 = \hbar \left\{ \left(n_1 + \frac{1}{2} \right) \sqrt{\lambda_1} + \left(n_2 + \frac{1}{2} \right) \sqrt{\lambda_2} + \left(n_3 + \frac{1}{2} \right) \sqrt{\lambda_3} \right\} \quad (48)$$

where λ_i 's are the roots of equation (19), while the eigenfunctions depend on ζ_i 's in the same way as they formerly depended on η_i 's. The variables ζ_i are defined by the transformation (18).

⁹ The estimation is founded on the formula $\int_{-\infty}^{+\infty} x^{2n} e^{-\alpha x^2} dx = \frac{(2n-1)(2n-3)\dots 1}{2^n \sqrt{\alpha^{2n+1}}} \sqrt{\pi}$.

Thus it is seen that the solution of the unperturbed Schrödinger equation reduces approximately to the problem of a three-dimensional anisotropic harmonic oscillator, in which the mass has been replaced by the principal moments of inertia, and the displacements by the variables η_i , ζ_i or ξ_i . These have, to a zero approximation, the significance of the angles of rotation about certain axes, and are in the simplest case identical with the principal axes of inertia. The result is thus a quantum correspondent of the classical theory of the torsional oscillations (Rousset 1944 b, 1945; Whittaker 1944. page 188), according to which such a motion can, to a first approximation, be regarded as a superposition of three harmonic torsional oscillations about the principal axes of inertia in case (16), and about the diameters, simultaneously conjugated with respect to both the ellipsoids (that of inertia and that of the directing momenta) in a general case.

VI. Estimation of the numerical value of the coefficients appearing in the equation. The introduction of assumptions I—V (in the preceding chapter), founded on relations (32), (36) requires a closer examination of how far they correspond to the real physical conditions. For this purpose may be used the experimental data pertaining to the „external Raman effect“ in molecular crystals (Rousset 1947). As an example the naphtalen monocystal has been chosen, with which the dispersion caused by the conjugation of the oscillations of the particular molecules in the crystal net is small, so that in the estimation the arithmetic mean of the frequency of the doublets may be taken as corresponding to the case in question of a single oscillator in the field of external forces (expressing the influence of the neighbouring molecules) The numerical data have been collected in Table I. The quantities measured are

B_i , $\tilde{\nu}_i = \frac{\nu_i}{c}$, whence u_{ii} 's are easily calculable. $u_{ij} = 0$ (for $i \neq j$), since the oscillations come to pass about the principal axes of inertia of the naphtalen molecule (fig. 2). According to these data

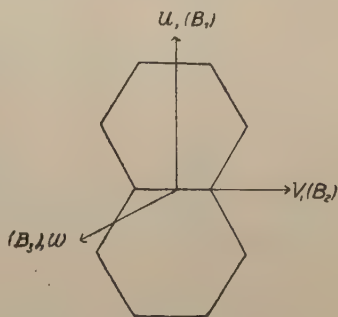


Fig. 2.

$$B_i a_i \geq 5 \cdot 10^2, \quad a_i \sim \gamma \cdot 10^3 \quad (49)$$

i	B_i	$\tilde{\nu}_i$	$\nu_i = \tilde{\nu}_i \cdot c$	$\omega_i = 2\pi\nu_i$ $= \sqrt{\frac{u_{ii}}{B_i}}$	ω_i^2	$\alpha_i = \frac{\omega_i}{\hbar_i}$	α_i^2	γ	γ^2	$\alpha_i B_i$	β_i $= 4\alpha_i B_i$
1	$2,2 \cdot 10^{-38} \text{ g.cm}^2$	118 cm^{-1}	$3,54 \cdot 10^{12} \text{ sec.}^{-1}$	$2,2 \cdot 10^{13}$	$4,8 \cdot 10^{26}$	$2,2 \cdot 10^{40}$	$4,8 \cdot 10^{80}$	$9,2 \cdot 10^{36}$	$8,4 \cdot 10^{73}$	$4,8 \cdot 10^2$	$1,9 \cdot 10^3$
3	$6,0 \cdot 10^{-38}$ "	75 "	$2,25 \cdot 10^{12}$ "	$1,4 \cdot 10^{13}$	$2,0 \cdot 10^{26}$	$1,4 \cdot 10^{40}$	$2,0 \cdot 10^{80}$	"	"	$8,4 \cdot 10^2$	$3,4 \cdot 10^3$
2	$8,4 \cdot 10^{-38}$ "	50 "	$1,50 \cdot 10^{12}$ "	$0,9 \cdot 10^{13}$	$0,9 \cdot 10^{26}$	$0,9 \cdot 10^{40}$	$0,9 \cdot 10^{80}$	"	"	$7,9 \cdot 10^2$	$9,2 \cdot 10^3$

Table I.

thus the conditions (32), (36) are really satisfied. More accurate calculations allow for an estimation of the upper limit of the errors (of the eigenvalues and -functions) deriving from the assumptions I-V. Assumption I: The error resulting from replacing the limits of integration $\pm 2\sqrt{B_i}$ by $-\infty + \infty$ is to be neglected (for $\eta_i = \pm 2\sqrt{B_i}$, $e^{-\frac{1}{2}\alpha_i \eta_i^2} \sim e^{-1000}$). Assumptions II and III: The errors of the mean values, calculated by using (37) and (40'), instead of (34) and (40), may be estimated jointly (they are of the same sign); the order of their magnitude can be grasped by comparing the normalizing factors in the two cases ($N_{n_1 n_2 n_3}$ and $N'_{n_1 n_2 n_3}$)

$$N_{n_1 n_2 n_3}^2 \int_{-\infty}^{+\infty} e^{-(\alpha_1 \eta_1^2 + \alpha_2 \eta_2^2 + \alpha_3 \eta_3^2)} H_{n_1}^2 H_{n_2}^2 H_{n_3}^2 d\eta_1 d\eta_2 d\eta_3 = 1 \quad (50)$$

$$I_{n_1 n_2 n_3} = N_{n_1 n_2 n_3}^2 \int_{-\infty}^{+\infty} e^{-[(\alpha_1 - \gamma) \eta_1^2 + (\alpha_2 - \gamma) \eta_2^2 + (\alpha_3 - \gamma) \eta_3^2]} H_{n_1}^2 H_{n_2}^2 H_{n_3}^2 \quad (50')$$

$$\left[1 + \frac{1}{8} \left(\frac{\eta_1^2}{B_1} + \frac{\eta_2^2}{B_2} + \frac{\eta_3^2}{B_3} \right) \right] d\eta_1 d\eta_2 d\eta_3 = 1 + \Delta_{n_1 n_2 n_3}$$

$$N'_{n_1 n_2 n_3} = \frac{N_{n_1 n_2 n_3}}{\sqrt{1 + \Delta_{n_1 n_2 n_3}}} \simeq N_{n_1 n_2 n_3} (1 - \frac{1}{2} \Delta_{n_1 n_2 n_3}) \quad (51)$$

$$\frac{1}{2} \Delta_{n_1 n_2 n_3} \simeq 0,9 \cdot 10^{-3} (n_1 + n_2 + n_3 + \frac{3}{2}). \quad (51')$$

Assumption IV. The relative error of the eigenvalues, resulting from the neglect of γ^2 in relation to α_i^2 , is of the order 10^{-6} . Assumption V. $E'' \simeq 10^{-3} \cdot E^0$.

The estimate made for naphtalen is founded merely on relations (32), (36), therefore it will hold for all the molecules satisfying these relations. They¹⁰ can be expressed in general in the form

$$\sqrt{B_i u_{ii}} \gg \hbar \quad (52)$$

or

$$B_i \tilde{v}_i \gg \frac{\hbar}{2\pi c} \simeq 5 \cdot 10^{-39}. \quad (53)$$

¹⁰ if B_i 's are of the same order. In the opposite case equation (52) corresponds to condition (32) only.

Since the moments of inertia of the molecules do not generally deviate excessively from values of order 10^{-38} g cm², and all the hitherto observed „external Raman lines“ are comprised within the limits $20 \text{ cm}^{-1} < \tilde{\nu} < 130 \text{ cm}^{-1}$ (whereby in a given molecule smaller frequencies correspond to larger momenta of inertia, and conversely) — so relation (52) will be satisfied generally. (53) renders it possible to test the applicability of the approximation on the basis of the experimental data in the particular cases.

VII. The perturbation calculus. The influence of terms of higher order, appearing in the kinetic energy but neglected in equation (15), can be taken into account by using a perturbation calculus (independent of time). These considerations have been carried out with the simplifying assumptions: (a) the oscillations take place about the principal axes of inertia, so that it is possible to compute in ξ_i -variables, (b) the eigenvalues of the oscillator are non-degenerate. (The calculations for other cases, in principle quite possible on the same assumptions, have been omitted because of considerable added complications). In accordance with the known formulae

$$E_n = E_n^0 + H'_{nn} \quad (54)$$

$$\psi_n = \psi_n^0 - \sum_{m=1}^{\infty} \frac{H'_{mn}}{E_m^0 - E_n^0} \psi_m^0 \quad (55)$$

$$H'_{mn} = \int \psi_m^0 H' \psi_n^0 d\tau. \quad (55')$$

According to relation (13)

$$\begin{aligned} H'\psi = -\frac{\hbar^2}{8} \sum_{1,2,3} \left\{ 2 \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \xi_1 \frac{\partial^2 \psi}{\partial \xi_2 \partial \xi_3} + \left[-\frac{1}{B_1} \xi_1^2 + \left(\frac{1}{B_3} - \frac{1}{B_1} \right) \xi_2^2 \right. \right. \\ \left. \left. + \left(\frac{1}{B_2} - \frac{1}{B_1} \right) \xi_3^2 \right] \frac{\partial^2 \psi}{\partial \xi_1^2} - \frac{2}{B_1} \xi_2 \xi_3 \frac{\partial^2 \psi}{\partial \xi_2 \partial \xi_3} - \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \xi_2 \xi_3 \frac{\partial \psi}{\partial \xi_1} \right\} \end{aligned} \quad (56)$$

or, on substituting for ψ the eigenfunctions of the unperturbed equation

$$\psi = \psi_1(\xi_1) \cdot \psi_2(\xi_2) \cdot \psi_3(\xi_3) \quad (57)$$

$$\psi_i = N_{n_i} e^{-\frac{1}{2} \eta_i^2} \cdot H_{n_i}(\eta) \quad (58)$$

$$\sqrt{\beta_i} \xi_i = \eta_i \quad (58')$$

$$\begin{aligned}
H'\psi = & -\frac{\hbar^2}{8} \sum_{1,2,3} \left\{ 2 \left(\frac{1}{B_2} - \frac{1}{B_3} \right) (\xi_1 \psi_1) \frac{d\psi_2}{d\xi_2} \frac{d\psi_3}{d\xi_3} - \frac{1}{B_1} \left(\xi_1^2 \frac{d^2\psi_1}{d\xi_1^2} \right) \psi_2 \psi_3 \right. \\
& + \left(\frac{1}{B_3} - \frac{1}{B_1} \right) \frac{d^2\psi_1}{d\xi_1^2} (\xi_2^2 \psi_2) \psi_3 \\
& + \left(\frac{1}{B_2} - \frac{1}{B_1} \right) \frac{d^2\psi_1}{d\xi_1^2} \psi_2 (\xi_3^2 \psi_3) - \frac{2}{B_1} \psi_1 \left(\xi_2 \frac{d\psi_2}{d\xi_2} \right) \left(\xi_3 \frac{d\psi_3}{d\xi_3} \right) \\
& \left. - \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \frac{d\psi_1}{d\xi_1} (\xi_2 \psi_2) (\xi_3 \psi_3) \right\}.
\end{aligned} \tag{56'}$$

The expressions of the types

$$\psi_i, \quad \xi_i \psi_i, \quad \xi_i^2 \psi_i, \quad \frac{d\psi_i}{d\xi_i}, \quad \xi_i \frac{d\psi_i}{d\xi_i}, \quad \frac{d^2\psi_i}{d\xi_i^2}, \quad \xi_i^2 \frac{d^2\psi_i}{d\xi_i^2}, \tag{59}$$

appearing in (56') can be transformed, by applying the known recurrence formulae for Hermite polynoms

$$\begin{aligned}
H'_n &= 2_n H_{n-1} \\
\rho H_n &= \frac{1}{2} H_{n+1} + n H_{n-1}
\end{aligned} \tag{60}$$

from which, after simple transformations, we obtain

$$\begin{aligned}
\xi \psi_n &= \frac{1}{\sqrt{\beta}} \left(\sqrt{\frac{n+1}{2}} \psi_n + \sqrt{\frac{n}{2}} \psi_{n-1} \right) \\
\xi^2 \psi_n &= \frac{1}{\beta} \left[\sqrt{\frac{n+1}{2}} \sqrt{\frac{n+2}{2}} \psi_{n+2} + \left(n + \frac{1}{2} \right) \psi_n + \sqrt{\frac{n}{2}} \sqrt{\frac{n-1}{2}} \psi_{n-1} \right] \\
\frac{\partial \psi_n}{\partial \xi} &= \sqrt{\beta} \left[-\sqrt{\frac{n+1}{2}} \psi_{n+1} + \sqrt{\frac{n}{2}} \psi_{n-1} \right] \\
\xi \frac{d\psi_n}{d\xi} &= -\sqrt{\frac{n+1}{2}} \sqrt{\frac{n+2}{2}} \psi_{n+2} - \frac{1}{2} \psi_n + \sqrt{\frac{n}{2}} \sqrt{\frac{n-1}{2}} \psi_{n-2} \\
\frac{d^2\psi_n}{d\xi^2} &= \beta \left[\sqrt{\frac{n+1}{2}} \sqrt{\frac{n+2}{2}} \psi_{n+2} - \left(n + \frac{1}{2} \right) \psi_n + \sqrt{\frac{n}{2}} \sqrt{\frac{n-1}{2}} \psi_{n-2} \right] \\
\xi^2 \frac{d^2\psi_n}{d\xi^2} &= \sqrt{\frac{n+1}{2}} \sqrt{\frac{n+2}{2}} \sqrt{\frac{n+3}{2}} \sqrt{\frac{n+4}{2}} \psi_{n+4} + \sqrt{n+1} \cdot \sqrt{n+2} \psi_{n-2} \\
&\quad - \frac{1}{2} \left(n^2 + n - \frac{1}{2} \right) \psi_n - \sqrt{n} \cdot \sqrt{n-1} \psi_{n-2} + \sqrt{\frac{n}{2}} \sqrt{\frac{n-1}{2}} \sqrt{\frac{n-2}{2}} \sqrt{\frac{n-3}{2}} \psi_{n-4}.
\end{aligned} \tag{61}$$

Inserting these expressions into (56') we can compute immediately the integrals (55'), making use of the orthogonality of the ψ -function ¹¹

$$\begin{aligned}
 H'_{mn} = & -\frac{\hbar^2}{8} \sum_{1,2,3} \left\{ -2 \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \sqrt{\frac{\beta_2 \beta_3}{\beta_1}} \cdot \sum_{(\varepsilon)} (K_1^\varepsilon \delta_{m_1 n_1 + \varepsilon}) \right. \\
 & \left. \sum_{(\varepsilon)} (K_2^\varepsilon \delta_{m_2 n_2 + \varepsilon}) \cdot \sum_{(\varepsilon)} (\varepsilon K_3^\varepsilon \delta_{m_3 n_3 + \varepsilon}) \right. \\
 & - \frac{1}{B_1} \left[\sum_{(\varepsilon)} M_1^\varepsilon \delta_{m_1 n_1 + 4\varepsilon} \delta_{m_2 n_2} \delta_{m_3 n_3} + 2\varepsilon L_1^\varepsilon \delta_{m_1 n_1 + 2\varepsilon} \delta_{m_2 n_2} \delta_{m_3 n_3} \right. \\
 & \left. \left. - \frac{1}{2} (n_1^2 + n_1 - \frac{1}{2}) \delta_{m_1 n_1} \delta_{m_2 n_2} \delta_{m_3 n_3} \right] \right. \\
 & + \left(\frac{1}{B_1} - \frac{1}{B_2} \right) \frac{\beta_2}{\beta_3} \delta_{m_1 n_2} \left[\sum_{(\varepsilon)} (L_2^\varepsilon \delta_{m_2 n_2 + 2\varepsilon}) - (n_2 + \frac{1}{2}) \delta_{m_2 n_2} \right] \\
 & \cdot \left[\sum_{(\varepsilon)} (L_3^\varepsilon \delta_{m_3 n_3 + 2\varepsilon}) + (n_3 + \frac{1}{2}) \delta_{m_3 n_3} \right] \\
 & + \left(\frac{1}{B_1} - \frac{1}{B_3} \right) \frac{\beta_3}{\beta_2} \delta_{m_1 n_1} \left[\sum_{(\varepsilon)} (L_2^\varepsilon \delta_{m_2 n_2 + 2\varepsilon}) + (n_2 + \frac{1}{2}) \delta_{m_2 n_2} \right] \\
 & \left[\sum_{(\varepsilon)} (L_3^\varepsilon \delta_{m_3 n_3 + 2\varepsilon}) - (n_3 + \frac{1}{2}) \delta_{m_3 n_3} \right] \\
 & + \frac{1}{2B_1} \delta_{m_1 n_1} \left[2 \sum_{(\varepsilon)} (\varepsilon L_2^\varepsilon \delta_{m_2 n_2 + 2\varepsilon}) + \delta_{m_2 n_2} \right] \left[2 \sum_{(\varepsilon)} (\varepsilon L_3^\varepsilon \delta_{m_3 n_3 + 2\varepsilon}) + \delta_{m_3 n_3} \right] \\
 & \left. + \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \sqrt{\frac{\beta_1}{\beta_2 \beta_3}} \sum_{(\varepsilon)} (\varepsilon K_1^\varepsilon \delta_{m_1 n_1 + \varepsilon}) \cdot \sum_{(\varepsilon)} (K_2^\varepsilon \delta_{m_2 n_2 + \varepsilon}) \cdot \sum_{(\varepsilon)} (K_3^\varepsilon \delta_{m_3 n_3 + \varepsilon}) \right\}
 \end{aligned} \tag{62}$$

where

$$\begin{aligned}
 K_i^\varepsilon &= \frac{1}{2} \sqrt{2n_i + 1 + \varepsilon} \\
 L_i^\varepsilon &= \frac{1}{4} \sqrt{(2n_i + 1 + \varepsilon)(2n_i + 1 + 3\varepsilon)} \\
 M_i^\varepsilon &= \frac{1}{16} \sqrt{(2n_i + 1 + \varepsilon)(2n_i + 1 + 3\varepsilon)(2n_i + 1 + 5\varepsilon)(2n_i + 1 + 7\varepsilon)}
 \end{aligned} \tag{63}$$

¹¹ $\sum_{1,2,3}$ denoting, as before, the sum of expressions resulting from the cyclic rearrangement of the indices 1, 2, 3; $\sum_{(\varepsilon)}$ denoting the sum of expressions for $\varepsilon = \pm 1$.

$$\varepsilon = \pm 1 \quad (63')$$

while δ_{mn} denotes Kronecker's symbol.

Writing $m_1 = n_1$, $m_2 = n_2$, $m_3 = n_3$ (the terms underlined once in formula (62)), we obtain a correction for the eigenvalues

$$E'_{n_1 n_2 n_3} = H'_{nn} = -\frac{\hbar^2}{8} \sum_{1,2,3} \left\{ \frac{1}{2B_1} \left(n_1^2 + n_1 - \frac{1}{2} \right) - \left[\left(\frac{1}{B_1} - \frac{1}{B_2} \right) \frac{\beta_2}{\beta_3} + \left(\frac{1}{B_1} - \frac{1}{B_3} \right) \frac{\beta_3}{\beta_2} \right] \left(n_2 + \frac{1}{2} \right) \left(n_3 + \frac{1}{2} \right) + \frac{1}{2B_1} \right\}. \quad (64)$$

Then, $E'_{n_1 n_2 n_3}$ is of the same order as the additional term E'' , derived from the terms containing the first derivative in the unperturbed equation (formula (46')). Combining the two terms and substituting the values for β_i 's (39), we finally obtain for the energy of the torsional oscillator, together with the correction, the formula

$$E_{n_1 n_2 n_3} = \hbar \sum_{1,2,3} \left\{ \left(n_1 + \frac{1}{2} \right) \omega_1 - \frac{\hbar^2}{16} \left[\frac{1}{B_1} \left(n_1 + \frac{1}{2} \right)^2 - 2 \left(\frac{B_1 - B_3}{B_2 B_3} \frac{\omega_1}{\omega_2} + \frac{B_2 - B_3}{B_1 B_3} \frac{\omega_2}{\omega_1} \right) \left(n_1 + \frac{1}{2} \right) \left(n_2 + \frac{1}{2} \right) - \frac{5}{4} \frac{1}{B_1} \right] \right\}. \quad (65)$$

In calculating the correction for the eigenfunctions, it suffices to take care only of the terms underlined twice in formula (62), since, as the numerical estimate¹² shows, the magnitude of the other terms (the number of which is finite) does not exceed 2 per cent of the value of the terms taken into account. Thus

$$H'_{mn} = \frac{\hbar^2}{4} \sum_{1,2,3} \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \sqrt{\frac{\beta_2 \beta_3}{\beta_1}} \sum_{(\varepsilon)} (K_1^\varepsilon \delta_{m_1 n_1 + \varepsilon}) \sum_{(\varepsilon)} (\varepsilon K_2^\varepsilon \delta_{m_2 n_2 + \varepsilon}) \cdot \sum_{(\varepsilon)} (\varepsilon K_3^\varepsilon \delta_{m_3 n_3 + \varepsilon}). \quad (66)$$

$H'_{mn} \neq 0$ for $m_i = n_i \pm 1$ ($i=1,2,3$) - altogether 8 possible combinations.

¹² Founded on the data for naphthalen, as before.

Denoting

$$J_1 = \left(\frac{1}{B_2} - \frac{1}{B_3} \right) \sqrt{\frac{\beta_2 \beta_3}{\beta_1}} = \frac{2}{\sqrt{h}} \frac{B_3 - B_2}{\sqrt{B_1 B_2 B_3}} \frac{\omega_2 \omega_3}{\sqrt{\omega_1 \omega_2 \omega_3}} \quad (67)$$

(1, 2, 3 cyclic rearrangements)

we obtain

$$H_{n_1 + \varepsilon_1, n_2 + \varepsilon_2, n_3 + \varepsilon_3} = \varepsilon_1 \varepsilon_2 \varepsilon_3 \frac{h^2}{4} (\varepsilon_1 J_1 + \varepsilon_2 J_2 + \varepsilon_3 J_3) \cdot K_1^{\varepsilon_1} K_2^{\varepsilon_2} K_3^{\varepsilon_3} \quad (68)$$

($\varepsilon_1, \varepsilon_2, \varepsilon_3$, assume the values ± 1). Hence, taking into account the significance of K_i^g we obtain from formula (55) the expression for the eigenfunctions of the torsional oscillator (together with the correction)¹³

$$\begin{aligned} \psi_{n_1 n_2 n_3} = & \psi_{n_1 n_2 n_3}^0 - \left\{ A_0 \left[\sqrt{\frac{n_1+1}{2}} \sqrt{\frac{n_2+1}{2}} \sqrt{\frac{n_3+1}{2}} \psi_{n_1+1, n_2+1, n_3+1}^0 \right. \right. \\ & \left. \left. - \sqrt{\frac{n_1}{2}} \sqrt{\frac{n_2}{2}} \sqrt{\frac{n_3}{2}} \psi_{n_1-1, n_2-1, n_3-1}^0 \right] \right. \\ & \left. + \sum_{1, 2, 3} A_1 \left[\sqrt{\frac{n_1+1}{2}} \sqrt{\frac{n_2}{2}} \sqrt{\frac{n_3}{2}} \psi_{n_1+1, n_2-1, n_3-1}^0 \right. \right. \\ & \left. \left. - \sqrt{\frac{n_1}{2}} \sqrt{\frac{n_2+1}{2}} \sqrt{\frac{n_3+1}{2}} \psi_{n_1-1, n_2+1, n_3+1}^0 \right] \right\} \quad (69) \\ A_0 = & \frac{\sqrt{h}}{2} \cdot \frac{(B_3 - B_2) \omega_2 \omega_3 + (B_1 - B_2) \omega_3 \omega_1 + (B_2 - B_1) \omega_1 \omega_2}{\sqrt{B_1 B_2 B_3} \sqrt{\omega_1 \omega_2 \omega_3} (\omega_1 + \omega_2 + \omega_3)} \\ A_1 = & \frac{\sqrt{h}}{2} \cdot \frac{-(B_3 - B_2) \omega_2 \omega_3 + (B_1 - B_3) \omega_3 \omega_1 + (B_2 - B_1) \omega_1 \omega_2}{\sqrt{B_1 B_2 B_3} \sqrt{\omega_1 \omega_2 \omega_3} (-\omega_1 + \omega_2 + \omega_3)}. \quad (69') \end{aligned}$$

Formulae (65), (69) give the result of the perturbation calculus. The practical significance of the correction obtained depends on its magnitude. According to the data for naphtalen, for the not very large n_i 's, $\Delta E_{n_1 n_2 n_3}$ does not exceed a few per cent of the unperturbed values $E_{n_1 n_2 n_3}^0$, and therefore is very small. To take it into account would be simply aimless, considering the magnitude of the errors resulting from the assumption I—V in the solution of the unperturbed equation. The energy levels of the torsional oscillator are thus closely approximated by the eigenvalues of the harmonic oscillator. The correction for the eigenfunctions (coefficients in the development (55)) does not exceed a few per cent — excluding the cases approaching degeneration of the type $\omega_1 + \omega_2 = \omega_3$.

¹³ For a case close to the degeneration of the type $\omega_1 + \omega_2 = \omega_3$ the correction becomes large. Such a case should be excluded from our considerations.

The perturbation calculus carried out here has been concerned only with the terms of higher order in kinetic energy. For the possible terms of higher order in potential energy we could make use of the results of considerations for the „translational“ oscillations (Herzberg 1945, page 204), from which it follows, for instance, that such a correction would have a form similar to (64), as far as the dependence on n_i 's is concerned. The coefficients, however, could not be fixed without accepting some closer assumptions as to the form of the potential energy.

VIII. Distribution of the orientation probabilities of the torsional oscillator. According to the statistical interpretation of quantum mechanics,

$$P = \psi^* \psi d\tau = \psi^2(\xi_1 \xi_2 \xi_3) d\tau = 8\sqrt{B_1 B_2 B_3} \psi^2 \cdot \sqrt{1 + \xi_1^2 + \xi_2^2 + \xi_3^2} d\xi_1 d\xi_2 d\xi_3 \quad (70)$$

expresses the probability that the variables ξ_1, ξ_2, ξ_3 assume the values within the element $d\tau$. Passing from the angles $\kappa_1, \kappa_2, \kappa_3$ to spherical coordinates (Section I, fig. 1) and taking the angles $\vartheta, \varphi, \varepsilon$ for independent variables we obtain immediately the probability of a determined spatial orientation

$$\left. \begin{aligned} \xi_1 &= \sin \vartheta \cos \varphi \sin \frac{\varepsilon}{2} \\ \xi_2 &= \sin \vartheta \sin \varphi \sin \frac{\varepsilon}{2} \\ \xi_3 &= \cos \vartheta \sin \frac{\varepsilon}{2} \end{aligned} \right\} \quad (71)$$

$$d\xi_1 d\xi_2 d\xi_3 = \frac{D(\xi_1 \xi_2 \xi_3)}{D(\vartheta \varphi \varepsilon)} d\vartheta d\varphi d\varepsilon = \frac{1}{2} \sin^2 \frac{\varepsilon}{2} \sin \vartheta d\vartheta d\varphi d\varepsilon \quad (72)$$

$$d\tau = 4\sqrt{B_1 B_2 B_3} \sqrt{1 + \sin^2 \frac{\varepsilon}{2} \sin^2 \frac{\varepsilon}{2} \cos^2 \frac{\varepsilon}{2}} \sin \vartheta d\vartheta d\varphi d\varepsilon \quad (73)$$

$$P = \psi^2(\vartheta \varphi \varepsilon) \cdot 4\sqrt{B_1 B_2 B_3} \sqrt{1 + \sin^2 \frac{\varepsilon}{2} \sin^2 \frac{\varepsilon}{2} \cos^2 \frac{\varepsilon}{2}} \sin \vartheta d\vartheta d\varphi d\varepsilon \quad (74)$$

In considerations confined to a zero approximation, the formula assumes a simpler form

$$P = \psi^2(\varepsilon_1, \varepsilon_2, \varepsilon_3) \sqrt{B_1 B_2 B_3} d\varepsilon_1 d\varepsilon_2 d\varepsilon_3 \quad (74')$$

(where $\varepsilon_i = 2\xi_i$ have the significance of the components of a small „vector of rotation“).

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FUNDAMENTAL POLARIZATION OF PHOTOLUMINESCENCE AND TORSIONAL VIBRATIONS OF MOLECULES

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A few introductory remarks are made concerning fundamental polarization of photoluminescence of solutions. The main assumptions and results of some known theories of fundamental polarization are recalled. The meaning of the term „spatial virtual electronic oscillator“, introduced in the writer's theory of fundamental polarization, is clearly stated and its usefulness advocated.

The well-known fact that the absolute values of the observed fundamental polarization are always smaller than those to be expected on the basis of reasonable theoretical considerations suggests the existence of some hitherto unnoticed depolarizing factors. The writer believes that these factors are: the torsional vibrations of luminescent molecules (considered as rigid bodies) about their equilibrium orientation in a surrounding solid medium, and possibly in some cases also torsional vibrations or rotations of parts of luminescent molecules and some of their normal vibrations. The first of these factors seems to be the most important and constitutes the main subject of the present paper.

It appears that the mean square of the angles of turn of the luminescent molecule carrying out torsional vibrations, plays an essential role in the present theory. An expression showing the dependence of this mean square on the temperature of the medium and on the frequency of torsional vibrations of the molecule as well as its moment of inertia is derived on the basis of the zeroth approximation of Hanus's theory of torsional oscillator. This approximation, valid for small amplitudes of torsional vibrations only, is assumed to be sufficiently good for present purposes. The theory is restricted to the most important case in which the excitation occurs in the absorption band involving electronic transition between the same pair of electronic levels as that involved in the emission of the photoluminescence band. Fundamental polarization in this particular case is called here „principal polarization“. Principal polarization, which results if the depolarization by torsional vibrations is taken into account after other depolarizing factors are excluded, is denoted here by „pseudoprincipal polarization“. An expression is derived for pseudoprincipal polarization as a function of the three principal transition probabilities of the virtual spatial electronic oscillator and the mean squares of the angles of turn about the three axes coinciding with the axes of the electronic oscillator. By means of this expression, the standard deviation of the angles of turn of the molecules, the frequency of their torsional vibrations and the corresponding moments of torsion, can be estimated (or in some particular cases even determined) on the basis of polar-

ization measurements. The theory is applied to the fluorescence of glyceric solutions of fuorescein and benzene.

Although the final experimental test of the theory must be awaited, the experimental facts so far known seem to corroborate it.

§ 1. Introduction. We shall call here „fundamental polarization“ P_0 , the rate of polarization¹ P of photoluminescence of an isotropic solution in which there are no depolarizing factors. The well-known depolarizing factors are: the thermal (Brown's) rotations of luminescent molecules and the migration of the excitation energy from one luminescent molecule to another. These factors can be avoided by choosing appropriate experimental conditions, or eliminated from experimental results by means of calculation. The value of P_0 can be predicted (at least in some cases) on the basis of reasonable considerations². It turns out, however that the experimental values of $|P_0|$ appear to be always smaller than those to be expected on the basis of these considerations. It seems reasonable to suspect the existence of some further depolarizing factors which have thus far escaped notice. The writer believes that these factors are: torsional vibrations of luminescent molecules (considered as rigid bodies) about their equilibrium orientation in the rigid surrounding medium (solvent), and in some cases torsional vibrations or even rotations of parts of molecules and some of their normal vibrations. The first of these factors seems to be the most important and is always present. It has already been treated in a preliminary note (Jabłoński 1950) and is the main subject of the present paper. Before we proceed to the theory of this effect we must recall briefly the main assumptions and results of some of the theories of fundamental polarization.

§ 2. The Theories of Fundamental Polarization. The limits between which the experimental values of fundamental polarization lie are: $-\frac{1}{3} < P_0 < +\frac{1}{2}$. It is important to note that in no case are these limits reached.

The earliest theory of fundamental polarization is due to Wawilow and Lewschin (1923). They assume a linear (i. e. totally aniso-

¹ The rate of polarization is defined as: $P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$ where I_{\parallel} and I_{\perp} are the intensity components of photoluminescence \parallel and \perp to the electric vector of the primary plane polarized light. The rate of depolarization ϱ is given by $\varrho = \frac{I_{\perp}}{I_{\parallel}} = \frac{1 - P}{1 + P}$. Hence $P = \frac{1 - \varrho}{1 + \varrho}$.

² Cf. page 204.

tropic) virtual electronic oscillator, rigidly connected with the luminescent molecule, the same oscillator being responsible for the absorption as well as for the emission of light. There results only one possible value of P_0 , viz. $P_0 = \frac{1}{2}$. Thus, their theory cannot explain the existence of cases in which P_0 is much smaller than $\frac{1}{2}$, or even negative. To remedy this defect, Perrin (1925–1929) assumes that in the general case, different linear oscillators are involved in the absorption and in the emission of light. P_0 depends on the angle α made by the directions of these oscillators. The limits of P_0 resulting from Perrin's theory are: $-\frac{1}{3} < P_0 < \frac{1}{3}$. Obviously, $\alpha \neq 0$ can be assumed only in cases in which absorption and emission involve transitions between different pairs of electronic levels. In cases in which the same pair of electronic levels is involved in both processes, $\alpha = 0$ must be assumed, the same oscillator being responsible for the absorption as well as for the emission of light. There again results $P_0 = \frac{1}{2}$ for this kind of excitation of photoluminescence.

Let us call henceforth „principal polarization“ the fundamental polarization in the cases in which the excitation occurs in the absorption band involving electronic transition between the same pair of electronic levels as that involved in the emission of the photoluminescence band. Let us denote the principal polarization by P_p .

The fact that in some cases P_p is much smaller than $\frac{1}{2}$ (Makowiecka 1934) induced the writer to propose a new theory in which spatial oscillators are introduced instead of linear oscillators (Jabłoński 1935, 1936). The main assumptions of this theory are: To every electronic transition belongs a particular oscillator. Each oscillator possesses in general three principal transition probabilities $\Gamma_1, \Gamma_2, \Gamma_3$ along three mutually perpendicular „principal“ axes³. The orientation of the axes of different oscillators with respect to the molecular axes is in general different. There are no fixed phase relations between the primary and the emitted light and no such relations between components along different principal axes of the electronic oscillator (the physical grounds for this assumption are given in previous papers (Jabłoński 1935, 1936)). The probability distribution of the directions of the transition moment responsible for the emission of light does not depend on the direction of the transition moment responsible for the absorption of light: The excited molecule „forgets“ the direction of the electric vector of the primary light. It follows from the above

³ Obviously, the linear oscillator constitutes a particular case of the spatial oscillator in which only one of the three principal transition probabilities is different from zero, say, $\Gamma_1 \neq 0$, $\Gamma_2 = \Gamma_3 = 0$.

assumptions that the transition probability along a direction making angles $\alpha_1, \alpha_2, \alpha_3$ with the directions of the principal transition probabilities is simply

$$G = \Gamma_1 \cos^2 \alpha_1 + \Gamma_2 \cos^2 \alpha_2 + \Gamma_3 \cos^2 \alpha_3. \quad (1)$$

Let us denote by $\Gamma_1, \Gamma_2, \Gamma_3$ the principal transition probabilities of the „absorption oscillator“ and by G_1, G_2, G_3 the „components“ of the transition probabilities of the „emission oscillator“ along the directions of the principal axes of the absorption oscillator (which can be calculated by means of (1)). Then, as was shown in a previous paper (Jabłoński 1950), the fundamental rate of depolarization is given by

$$\varrho_0 = \frac{2 \sum_{j=1}^3 \sum_{k=1}^3 \Gamma_j G_k - \sum_{i=1}^3 \Gamma_i G_i}{\sum_{j=1}^3 \sum_{k=1}^3 \Gamma_j G_k + 2 \sum_{i=1}^3 \Gamma_i G_i}. \quad (2)$$

Hence the rate of fundamental polarization is

$$P_0 = \frac{1 - \varrho_0}{1 + \varrho_0} = \frac{3 \sum_{i=1}^3 \Gamma_i G_i - \sum_{j=1}^3 \sum_{k=1}^3 \Gamma_j G_k}{\sum_{i=1}^3 \Gamma_i G_i + 3 \sum_{j=1}^3 \sum_{k=1}^3 \Gamma_j G_k}. \quad (2a)$$

We obtain the principal depolarization from (2) by setting $G_1 = \Gamma_1, G_2 = \Gamma_2, G_3 = \Gamma_3$

$$\varrho_p = \frac{2 \left(\sum_{j=1}^3 \Gamma_j \right)^2 - \sum_{i=1}^3 \Gamma_i^2}{\left(\sum_{j=1}^3 \Gamma_j \right)^2 + 2 \sum_{i=1}^3 \Gamma_i^2}, \quad (3)$$

and similarly the principal polarization from (2a)

$$P_p = \frac{3 \sum_{i=1}^3 \Gamma_i^2 - \left(\sum_{j=1}^3 \Gamma_j \right)^2}{\sum_{i=1}^3 \Gamma_i^2 + 3 \left(\sum_{j=1}^3 \Gamma_j \right)^2}. \quad (3a)$$

These formulae were given in a somewhat different but thoroughly equivalent form in the original paper⁴. This new form seems to fit better the considerations given in the next sections.

⁴ Aside from the form of the formulae, different notations were also used (A_i^2 instead of Γ_i^2 and B_i^2 instead of G_i^2).

Inspection of (2) and (2 a) shows that

$$\frac{1}{3} \leq \varrho_0 \leq 2, \quad \text{or} \quad -\frac{1}{3} \leq P_0 \leq \frac{1}{2}. \quad (4)$$

The limits of possible values of the principal depolarization and the principal polarization resulting from (3) and (3 a) are

$$\frac{1}{3} \leq \varrho_p \leq 1, \quad \text{or} \quad 0 \leq P_p \leq \frac{1}{2}. \quad (5)$$

Since all the experimental values of P_p lie within the limits given by (5), the main difficulty of the previous theories of polarization is thus removed.

It must be emphasized that only the relative values of the principal transition probabilities in (2), (2 a), (3) and (3 a) are relevant.

Setting in (3 a) $\Gamma_1 \neq 0$, $\Gamma_2 = \Gamma_3 = 0$ (the case of a linear oscillator), we obtain $P_p = \frac{1}{2}$.

Setting $\Gamma_1 = \Gamma_2 \neq 0$, $\Gamma_3 = 0$ (the case of a plane symmetrical oscillator), we obtain $P_p = \frac{1}{4}$.

In the case of $\Gamma_1 = \Gamma_2 = \Gamma_3 \neq 0$ (spherical oscillator), we obtain $P_p = 0$.

Equations (2), (2 a), (3) and (3 a) were derived under the assumption of non-existence of any depolarizing factors. The influence of rotations of molecules on polarization of photoluminescence is satisfactorily described by the theory of Perrin (1925—1929). The influence of the torsional vibrations (always existing) will be treated in § 4.

We shall now discuss the compatibility of the assumption of spatial virtual oscillators with the theory of molecular spectra. Let us quote a passage from an article of Sponer and Teller (1941): „Electronic transition probabilities are determined by the matrix elements of the dipole moment $\int \psi'_{el}^* M \psi''_{el} d\tau_{el}$. Here ψ'_{el} and ψ''_{el} are the electronic eigenfunctions in the upper and lower states; the asterisk (ψ'^*) indicates the conjugate complex value. M is the dipole of the system of nuclei and electrons for a definite electronic configuration. The integration must be carried out over all configuration of the electrons (symbolically indicated by the volume element $d\tau_{el}$)... A general group theoretical argument shows that $\int \psi'_{el}^* M \psi''_{el} d\tau_{el}$ can be different from zero only if the direct product of the transformation properties of separate factors contains a totally symmetrical term (i. e., one that remains unchanged during all symmetry operations). One can prove moreover that the above condition is equivalent to the requirement that the direct product of the term symbols belonging to ψ'_{el} and ψ''_{el} should contain a term with the transformation properties of M . The latter transforms in the same way as a translation. Therefore the following

general statement can be made: A combination between two states is allowed if their direct product contains a term which transforms like one of the translations T_x , T_y or T_z . The direction of this translation determines the direction of the dipole moment connected with transition (transition moment)". In the light of the above passage we might think that the introduction of linear virtual oscillators is the only legitimate one. In order to elucidate this point, the meaning of the expression „spatial virtual electronic oscillator“ must be clearly stated. It does not apply to an actual individual transition but rather to a set of possible electronic transitions between two (in general degenerate) levels or between two groups of very close levels giving rise to one (or practically one) absorption or photoluminescence band⁵. In this case the transition moments may assume different directions with respect to molecular axes.

The same applies to the molecules in which the transition forbidden by symmetry is made permissible by transient factors (e.g. by excitation of non-totally symmetrical vibrations of nuclei). In this case the anisotropy of the virtual electronic oscillator is determined by the symmetry of the molecule alone. As an example we may quote the fluorescence of benzene (in solutions) which is due to an electronic transition moment parallel to the plane of the molecule. This case corresponds exactly to a plane symmetrical electronic oscillator with two of its principal transition probabilities equal, and the third equal to zero (say: $\Gamma_1 = \Gamma_2 \neq 0$; $\Gamma_3 = 0$).

It is important to remember that the theory applies to molecules surrounded by a condensed medium only. The disturbances caused by this medium play an essential role in the phenomena described by it. Owing to these disturbances, the probability distribution of the directions of the transition moments involved in the emission of light in a molecule, can be assumed to be independent of the direction of the transition moment involved in the absorption of light. The same cause produces the phase independence already mentioned. Further effects produced by the same cause (e.g. the displacement of the luminescence band with respect to the absorption bands) were treated in some of the previous papers (Jabłoński 1931, 1935, 1936) but are irrelevant in the present investigation.

The above considerations may suffice to show the usefulness of the theory of polarization based on the assumption of spatial oscillators and its compatibility with the theory of molecular spectra.

⁵ Thus, in general several pairs of electronic eigenfunctions are involved in one spatial oscillator.

§ 3. Torsional Vibrations of Molecules. The quantum mechanical theory of torsional vibrations of molecules was developed by Pauling (1930), Stern (1931) and Hanus (1951). As shown by Mrs. Hanus, the total torsional vibration of a molecule (treated as a rigid body) can be described in the case of small amplitudes by means of three approximately independent torsional vibrations about three certain axes fixed in space (zeroth approximation). These axes coincide with the principal axes of inertia of the molecule (in its equilibrium orientation). The most important case is that in which the axes of the ellipsoid of moment of torsion have the same direction as the principal axes of inertia. We shall confine ourselves to this case only. Each of the three vibrations is described by a Schrodinger equation of the harmonic oscillator, in which the mass is substituted by the moment of inertia I_i and the displacement by the angle of turn ε_i about the corresponding axis. The three (angular) eigenfrequencies are

$$\omega_i = \sqrt{\frac{\tau_i}{I_i}}, \quad i = 1, 2, 3, \quad (6)$$

where τ_i are the principal moments of torsion and I_i the principal moments of inertia of the molecule.

The corresponding eigenvalues (in the zeroth approximation) are

$$E_i = (n_i + \frac{1}{2}) \omega_i \hbar, \quad n_i = 0, 1, 2, 3, \dots \quad (7)$$

The eigenfunctions are

$$\psi_{n_i} = \left(\frac{\beta_i}{\pi}\right)^{\frac{1}{4}} (n_i! 2^{n_i})^{-\frac{1}{2}} e^{-\frac{\beta_i \varepsilon_i^2}{2}} H_{n_i}(\sqrt{\beta_i} \varepsilon_i), \quad (8)$$

where $\beta_i = \frac{I_i \omega_i}{\hbar}$, H_{n_i} are the Hermitian polynomials. In the same approximation the total energy is

$$E_{n_1, n_2, n_3} = E_1 + E_2 + E_3 = \hbar[(n_1 + \frac{1}{2})\omega_1 + (n_2 + \frac{1}{2})\omega_2 + (n_3 + \frac{1}{2})\omega_3], \quad (9)$$

and the total eigenfunction

$$\psi_{n_1, n_2, n_3} = \psi_{n_1}(\varepsilon_1) \psi_{n_2}(\varepsilon_2) \psi_{n_3}(\varepsilon_3). \quad (10)$$

As shown by Mrs. Hanus, the zeroth approximation (in which the non-separable terms in the full Schrodinger equation are neglected) is rather good for small quantum numbers n_i . Although it becomes worse for larger quantum numbers, we shall nevertheless use this approximation only throughout.

What we need in applications to the theory of polarization are the mean squares of each of the three angles of turn $\bar{\varepsilon}_i^2$ of luminescent molecules in a solid solution in thermal equilibrium at a given temperature $T^0 K$.

Let us first calculate this mean square for a particular vibration state, say n_i . Let us denote it by $\bar{\varepsilon}_{n_i}^2$. There results from (8) ⁶:

$$\bar{\varepsilon}_n^2 = \int_{-\infty}^{+\infty} \varepsilon_n^2 \psi_n^2 d\varepsilon_n = (n + \frac{1}{2}) \frac{1}{\beta} = (n + \frac{1}{2}) \frac{\hbar}{I\omega} \quad (11)$$

(we have dropped the subscripts $., i$!).

Now, $(n + \frac{1}{2}) \hbar / I\omega = E_n / I\omega^2$, hence

$$\bar{\varepsilon}_n^2 = \frac{E_n}{I\omega^2}, \quad (12)$$

E_n being the energy of the torsional vibrations in the state n_i .

In order to obtain the mean square $\bar{\varepsilon}_i^2$ in the case of thermal equilibrium at temperature $T^0 K$ (when different quantum states of vibration are excited) we must substitute in (12), not the energy of a particular state but instead the mean value of the energy of an harmonic oscillator at this temperature (including its zero point energy):

$$\bar{E} = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\frac{\hbar \omega}{kT}} - 1}.$$

Finally we obtain

$$\bar{\varepsilon}_i^2 = \frac{\hbar}{I\omega} \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar \omega}{kT}} - 1} \right). \quad (13)$$

Thus, molecules in solid media carry out torsional vibrations even at $T = 0^0 K$ ($\bar{\varepsilon}_i^2 = \hbar / 2I\omega$).

Provided I_i and T are given, (13) enables us to evaluate $\bar{\varepsilon}_i^2$ if ω_i is known, or to evaluate ω_i if $\bar{\varepsilon}_i^2$ is known ⁷.

⁶ Cf. e. g. H. Margenau and G. M. Murphy (1943).

⁷ From the investigations of the external Raman effect the eigenfrequencies of torsional vibrations of some molecules in crystals were obtained. Using the results of Rousset (1947) for naphtalene molecules in pure naphtalene crystals we have calculated by means of (13) the standard deviations of angles of turn $\sqrt{\bar{\varepsilon}_i^2}$ for the torsional vibrations of that molecule about its three principal axes of inertia. The results are given in table I. The eigenfrequencies quoted there are the mean values

§ 4. Influence of Torsional Vibrations on P_p . Any orientation of a molecule differing from its equilibrium orientation may be described by means of an angle of turn about a suitable axis. In the case of small angles of turn (to which we shall restrict ourselves) they can be treated approximately as vectors and thus described by their components along the axes of a co-ordinate system fixed in space. In this approximation the angle of turn resulting from several successive turns does not depend on the order in which they are carried out.

Let us consider a solution of luminescent molecules with principal transition probabilities Γ_1 , Γ_2 and Γ_3 (the same for absorption as for emission). The principal polarization is given by (3 a):

$$P_p = \frac{3 \sum_i \Gamma_i^2 - (\sum_j \Gamma_j)^2}{\sum_i \Gamma_i^2 + 3 (\sum_j \Gamma_j)^2} \quad (14)$$

The „pseudoprincipal polarization“, i. e. the polarization which results from the principal polarization if depolarization by the torsional vibrations of luminescent molecules is taken into account, can be expressed by a similar formula in which Γ_i are replaced by Γ'_i which are the mean values of the transition probabilities along the directions of the axes of the principal transition probabilities in their equilibrium orientations. The torsional vibrations tend to equalize these transition probabilities. Let us denote the pseudoprincipal polarization by P'_p .

of the frequencies of Raman doublets (the cause of doubling has been explained by Rousset).

Table I. *Standard deviations of angles of turn of a naphthalene molecule in pure naphthalene crystals*

Axis	1	2	3
$I_i \cdot 10^{38}$	2,2	6,0	8,4
$\omega_i \cdot 10^{13}$	2,2	1,4	0,94
$\sqrt{\epsilon_i^2}$ at 0°K	2°	1°26'	1°27'
$\sqrt{\epsilon_i^2}$ at 300°K	3°47'	3°38'	4°15'
$\tau_i \cdot 10^{11}$	1,01	1,18	0,74

The data given in different columns refer to the axes $i = 1, 2$ and 3 respectively; $\tau_i = I_i \omega_i^2$ is the moment of torsion responsible for the vibrations about the corresponding axis τ_i and I_i are in *cgs* units.

By means of (1) we have

$$\Gamma'_1 = \Gamma_1 \overline{\cos^2 \alpha_{11}} + \Gamma_2 \overline{\cos^2 \alpha_{12}} + \Gamma_3 \overline{\cos^2 \alpha_{13}}, \dots, \quad (15)$$

where α_{ij} are the angles made by Γ_j with the equilibrium direction of Γ_i and $\overline{\cos^2 \alpha_{ij}}$ are mean values of $\cos^2 \alpha_{ij}$.

Let θ_1 , θ_2 and θ_3 be the angles of turn about the equilibrium directions of Γ_1 , Γ_2 and Γ_3 and $\theta_1 \ll 1$, $\theta_2 \ll 1$, $\theta_3 \ll 1$. Then

$$\begin{aligned} \overline{\cos^2 \alpha_{11}} &\approx \overline{\cos^2 \theta_2 \cos^2 \theta_3} \approx 1 - \overline{\theta_2^2} - \overline{\theta_3^2}, \dots, \\ \overline{\cos^2 \alpha_{12}} &\approx \overline{\cos^2 \alpha_{21}} \approx \overline{\theta_3^2}, \dots, \end{aligned} \quad (16)$$

From (15) and (16) we obtain

$$\Gamma'_1 = \Gamma_1 + (\Gamma_2 - \Gamma_1) \overline{\theta_3^2} + (\Gamma_3 - \Gamma_1) \overline{\theta_2^2}, \dots, \quad (17)$$

Inspection of (17) shows that $\sum_i \Gamma'_i = \sum_i \Gamma_i$, i. e. the sum of transition probabilities is not changed by torsional vibrations (as it must be in fact). If the axes of the electronic oscillator and those of the torsional oscillator coincide, we have to put $\overline{\theta_i^2} = \overline{\varepsilon_i^2}$, where $\overline{\varepsilon_i^2}$ are the mean squares of angles of turn about the axes of the torsional oscillator.

If this is not the case $\overline{\theta_i^2}$ are functions of $\overline{\varepsilon_j^2}$ (or of a part of them). Let β_{ij} be angles made by the (mutually perpendicular) axes of the torsional oscillator with those of the electronic oscillator (the first subscript referring to the axes of the electronic oscillator the second to those of the torsional oscillator). Then

$$\overline{\theta_i^2} = \overline{(\sum_j \varepsilon_j \cos \beta_{ij})^2} = \sum_j \overline{\varepsilon_j^2} \cos^2 \beta_{ij}, \quad (i=1, 2, 3) \quad (18)$$

since in our approximation $\overline{\varepsilon_i \varepsilon_j} = 0$ for $i \neq j$.

Substituting Γ'_i (17) for Γ_i in (14) we obtain the following expression for the pseudoprincipal polarization

$$P'_p = \frac{3 \sum_i \Gamma_i'^2 - (\sum_i \Gamma_i')^2}{\sum_i \Gamma_i'^2 + 3(\sum_i \Gamma_i')^2}, \quad (19)$$

since $\sum_j \Gamma'_j = \sum_j \Gamma_j$.

Let us now apply (19) and (17) to some simple particular cases. It has already been done in the preliminary note (Jabłoński 1950) but it seems expedient to quote it here for the sake of completeness.

Let the oscillator be linear ($\Gamma_1 = 1$, $\Gamma_2 = \Gamma_3 = 0$) and let ⁸
 $\overline{\theta_2^2} = \overline{\theta_3^2} = u/2$; $\overline{\theta_1^2}$ is irrelevant in this case. Putting these values of Γ_i^1
 and $\overline{\theta_i^2}$ into (17), we obtain $\Gamma_1' = 1 - u$, $\Gamma_2' = \Gamma_3' = u/2$; hence by means
 of (19) ⁹

$$P_p' = \frac{9u^2 - 12u + 4}{3u^2 - 4u + 8}. \quad (20)$$

Another simple case is that of a flat symmetrical oscillator ($\Gamma_1 = 0$,
 $\Gamma_2 = \Gamma_3$). Again let $\overline{\theta_2^2} = \overline{\theta_3^2} = u/2$; $\overline{\theta_1^2}$ is irrelevant. From (17) and (19)
 we have

$$P_p' = \frac{9u^2 - 12u + 4}{3u^2 - 4u + 28}. \quad (21)$$

Now the question arises whether it is possible to obtain the three
 eigenfrequencies of torsional vibrations from measurements of the
 pseudoprincipal polarization. Inspection of (17) and (19) shows that
 it is impossible in the general case in which all these frequencies are
 different. In general only a very rough estimate of the order of magni-
 tude of something like a mean value of the three frequencies can be
 made, if all $\overline{\theta_i^2}$ in (17) are considered to be equal ($\overline{\theta_1^2} = \overline{\theta_2^2} = \overline{\theta_3^2} = \delta$), and
 if the anisotropy of the electronic oscillator can be assumed as known
 a priori. By means of (19) we then can evaluate δ on the basis of the
 experimental value of P_p' . Using this value of $\delta = \overline{\varepsilon^2}$ and the mean
 value of principal moments of inertia of the molecule, we can calculate
 by means of (13) the frequency which is the „mean value“ of the three
 frequencies of torsional vibration of the molecule¹⁰. We shall now
 derive an expression which makes the evaluation of δ on the basis
 of P_p and P_p' very easy.

From (14) and (19) we have

$$\frac{\sum_i \Gamma_i^2}{(\sum_i \Gamma_i)^2} = \frac{10}{3 - P_p} - 3 \quad (14 a)$$

and

$$\frac{\sum_i \Gamma_i'^2}{(\sum_i \Gamma_i')^2} = \frac{10}{3 - P_p'} - 3. \quad (19 a)$$

⁸ This is a rather exceptional case. In general $\overline{\theta_2^2} \neq \overline{\theta_3^2}$.

⁹ Cf. also the formula (20) of Perrin's paper (1929).

¹⁰ Even this rough estimate must be made with caution. One must make
 sure that no other factors apart from torsional vibrations affect appreciably the
 rate of polarization.

There from there results

$$\frac{\sum_i (\Gamma_i^2 - \Gamma_i'^2)}{(\sum_i \Gamma_i)^2} = 10 \left(\frac{1}{3 - P_p} - \frac{1}{3 - P_p'} \right). \quad (22)$$

Putting $\bar{\theta}_1^2 = \bar{\theta}_1'^2 = \bar{\theta}_3^2 = \delta$ in (17) we obtain

$$\Gamma_i' = \Gamma_i(1 - 3\delta) + \delta \sum_j \Gamma_j, \quad (i=1, 2, 3). \quad (23)$$

Hence

$$\frac{\sum_i (\Gamma_i^2 - \Gamma_i'^2)}{(\sum_j \Gamma_j)^2} = (2\delta - 3\delta^2) \left[\frac{3 \sum_i \Gamma_i^2}{(\sum_j \Gamma_j)^2} - 1 \right]. \quad (24)$$

From (24), (14 a) and (22) we obtain the final expression

$$3\delta^2 - 2\delta + \frac{P_p - P_p'}{P_p(3 - P_p')} = 0. \quad (25)$$

Using Perrin's (1925—1929) value of pseudoprincipal polarization of fluorescence of fluorescein in glyceric solution at $T = 300^\circ \text{K}$: $P_p' = 0,44$, and assuming $P_p = 0,5$, we obtain by means of (25): $\delta = 0,025$. This corresponds to a standard deviation of the angle of turn in the above conditions $\sqrt{\delta} = \sqrt{\bar{\theta}^2} = 0,158 = 9^\circ$ (this is merely a „mean value“ in the meaning given above).

Assuming $P_p = 1/7$ for the benzene molecule (symmetrical flat electronic oscillator) and using Feofilov's (1947) value $P_p' = 1/14$ for benzene in glyceric solution at $T = 263^\circ \text{K}$, we have $\delta = 0,111$ and the standard deviation $\sqrt{\delta} = 0,334 = 19^\circ$.

In some (rather exceptional) cases the measurements of polarization can provide us with more exact information about the mean squares of the angles of turn and even about frequencies of torsional vibrations than is possible in the general case.

If we can consider a priori two of the $\bar{\theta}_i^2$ as equal and the third one as irrelevant, we can evaluate the two equal relevant $\bar{\theta}_i^2$ by means of (19) or (25). If, besides, the corresponding (equal) moments of inertia of the molecule and the orientation of the electronic oscillator with respect to the axes of the torsional oscillator are known, the frequency of the relevant torsional vibrations can be calculated by means of (13). These conditions are fulfilled in the case of the benzene molecule. Any pair of mutually perpendicular axes lying in the plane of this molecule may be considered as the axes of a flat symmetrical electronic oscillator ($\Gamma_1 = \Gamma_2 \neq 0$, $\Gamma_3 = 0$) as well as the relevant principal axes

of inertia (with equal moments of inertia $I_1 = I_2 = 1,45 \cdot 10^{-38}$ gr cm²)¹¹. Thus, the value of δ calculated above ($\delta = \theta^2 = \varepsilon^2 = 0,111$) is the mean square of the angles of turn for torsional vibrations about any axis lying in the plane of the benzene molecule under the conditions quoted above. The calculation made by means of (13) leads to $\tilde{\nu} = 26$ cm⁻¹ for the wave number of torsional vibrations of the benzene molecule in glyceric solution about any axis lying in the plane of the molecule¹². There results the corresponding moment of torsion

$$\tau = I\omega^2 = 3,4 \cdot 10^{-13} \text{ cm}^2 \cdot \text{gr} \cdot \text{sec}^{-2}.$$

The wave numbers of torsional vibrations found by Rousset¹² from investigation of the external Raman effect in pure benzene crystals are $\tilde{\nu} = 60$ and 100 cm⁻¹ (doublet). As should be expected, the frequency in solution appears to be smaller than those in a pure benzene crystal. However, the order of magnitude is the same.

§ 5. Concluding Remarks. The experimental results so far available seem to corroborate the present theory at least qualitatively. In order to test all the conclusions of the theory quantitatively, special investigations will be needed. For the time being we can already state with safety that one of the conclusions which can be drawn from the theory is established by experimental facts. This conclusion is: The experimental methods used so far lead, not the determination of principal polarization, but to the determination of the pseudoprincipal polarization i. e. of the principal polarization diminished by the torsional vibrations of molecules and possibly by the further depolarizing factors quoted in § 1.

So far there is no experimental evidence available concerning the dependence on temperature of the effect caused by torsional vibrations on the polarization and no such evidence exists concerning the existence of this effect at 0° K.

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¹¹ The torsional vibration or even rotation about the third axis perpendicular to the plane of the molecule cannot produce any depolarisation.

¹² We have disregarded here the possible dependence of $\tilde{\nu}$ on the temperature (i. e. considered the moments of torsion as constant) and neglected the possible splitting of the levels due to the degeneracy. Moreover, we have assumed the whole depolarization to be due to the torsional vibrations only. For the time being it is difficult to decide how far these simplifications are justified.

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NON LINEAR EFFECTS IN THE THEORY OF QUANTIZED FIELDS II ¹.

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In this paper elements of the Heisenberg S-matrix for the process of scattering of light by light under the assumption of interaction with charged scalar meson field are calculated. The calculations are based on Feynman and Dyson's invariant technique of calculations, described in the first part of this paper.

1. Introduction

In the present paper the scattering of light by light is studied under the assumption of interaction of the photon field with scalar or pseudoscalar charged meson field. This interaction exists even in the absence of actual scalar or pseudoscalar particles. We shall treat the case when two primary photons produce two secondary ones by applying the relativistically invariant technique of calculation of Feynman and Dyson described in I. The lowest order of approximation giving non-vanishing results is the forth. In this approximation infinities do not appear and there it no need to introduce any renormalization in the interaction hamiltonian. Our results will also apply, with a slight modification, to the case of a single photon breaking up into three parallel photons.

2. The scattering between two photons

The interaction energy between a scalar meson field and a photon field is

$$h = f + g, \quad (1)$$

where

$$f = -e\lambda A_\lambda, \quad g = e^2 \psi^* \psi A_i^2 \quad (2)$$

¹ The first part of this paper being Jerzy Rayski, *Non Linear Effects in the Theory of Quantized Fields I*, which will be referred to as I.

and

$$s_\lambda = ie(\psi_\lambda^* \psi - \psi_\lambda \psi^*) \quad (3)$$

ψ is the field variable of the scalar meson field, $\psi_\lambda = \frac{\partial \psi}{\partial x_\lambda}$; A_λ is the field variable of the photon field. The commutation relations for these two fields are

$$[\psi(1), \psi^*(2)] = i\Delta(1, 2), \quad [A_\mu(1), A_\nu(2)] = i\delta_{\mu\nu} D(1, 2). \quad (4)$$

The Schrödinger equation takes here the form (see I, (4), (4'), (4''))

$$\dot{\Psi} = -i(H + G)\Psi, \quad (5)$$

where

$$H = \int d^3x f, \quad G = \int d x g.$$

We assume a state fixed by the requirement that for $t = -\infty$ there exist two photons and no scalar meson, and look for the probability of finding, for $t = +\infty$, again two photons and no scalar meson.

The elements of the S -matrix of Heisenberg

$$\Psi(\infty) = S\Psi(-\infty) = (1 + R)\Psi(-\infty), \quad (6)$$

which are responsible for this scattering, are found by the usual perturbation treatment and assume the form

$$\begin{aligned} R = & (-i)^4 \int_{t_1 > t_2 > t_3 > t_4} d^4x_1 d^4x_2 d^4x_3 d^4x_4 f(1) f(2) f(3) f(4) \\ & + (-i)^3 \int_{t_1 > t_2 > t_3} d^4x_1 d^4x_2 d^4x_3 (f(1) f(2) g(3) + f(1) g(2) f(3) + g(1) f(2) f(3)) \\ & + (-i)^2 \int_{t_1 > t_2} d^4x_1 d^4x_2 g(1) g(2). \end{aligned}$$

Introducing the symbol P of Dyson, we get

$$\begin{aligned} R = & \frac{(-i)^4}{4!} \int d^4x_1 \dots d^4x_4 P(f(1) \dots f(4)) + \\ & + \frac{(-i)^3}{3!} \int d^4x_1 d^4x_2 d^4x_3 P(f(1) f(2) g(3)) \\ & + \frac{(-i)^2}{2!} \int d^4x_1 d^4x_2 P(g(1) g(2)). \end{aligned}$$

The order of the functions A_λ is immaterial, since if we change the order of the A_i we get additional terms with a diminished number of A_3 's which contribute nothing to our problem. Therefore we may replace $P(A_\lambda(1) A_\mu(2) A_\nu(3) A_\pi(4))$ by $A_\lambda(1) A_\mu(2) A_\nu(3) A_\pi(4)$ etc.

Now we must take the vacuum expectation value of the following expressions

$$\begin{aligned} \langle P(s_\lambda(1) s_\mu(2) s_\nu(3) s_\pi(4)) \rangle_0, \quad \langle P(s_\lambda(1) s_\mu(2) \psi^*(3) \psi(3)) \rangle_0 \\ \langle P(\psi^*(1) \psi(1) \psi^*(2) \psi(2)) \rangle_0. \end{aligned} \quad (8)$$

We begin with the calculation of the first term. According to (3) we have for any sequences of time variables (see I)

$$\begin{aligned} \langle P(s_\lambda(1) s_\mu(2) s_\nu(3) s_\pi(4)) \rangle_0 = \\ = \langle (\psi_\lambda^*(1) \psi(1) - \psi_\lambda(1) \psi^*(1)) \cdot (\psi_\mu^*(2) \psi(2) - \psi_\mu(2) \psi^*(2)) \cdot \\ \cdot (\psi_\nu^*(3) \psi(3) - \psi_\nu(3) \psi^*(3)) \cdot (\psi_\pi^*(4) \psi(4) - \psi_\pi(4) \psi^*(4)) \rangle_0. \end{aligned} \quad (9)$$

Let us take e. g. the first of the 16 terms appearing in (9)

$$\langle \psi_\lambda^*(1) \psi(1) \psi_\mu^*(2) \psi(2) \psi_\nu^*(3) \psi(3) \psi_\pi^*(4) \psi(4) \rangle_0$$

which may be written in the following form

$$\begin{aligned} \langle \psi_\lambda^*(1) \psi(2) \rangle_0 \langle \psi_\mu^*(2) \psi(4) \rangle_0 \langle \psi(1) \psi_\nu^*(3) \rangle_0 \langle \psi(3) \psi_\pi^*(4) \rangle_0 \cdot \\ + \langle \psi(1) \psi_\mu^*(2) \rangle_0 \langle \psi_\lambda^*(1) \psi(3) \rangle_0 \langle \psi(2) \psi_\pi^*(4) \rangle_0 \langle \psi_\nu^*(3) \psi(0) \rangle_0 + \text{etc.}, \end{aligned} \quad (10)$$

where all the permutations of 1, 2, 3, 4, should be taken into account except the reversing of the order of terms such as $\langle \psi(i) \psi^*(j) \rangle_0$ and $\langle \psi^*(i) \psi(j) \rangle_0$. Introducing the well-known formulae for vacuum expectation values

$$\begin{aligned} \langle \psi(1) \psi^*(2) \rangle_0 = i\Delta^+(1,2), \quad \langle \psi^*(2) \psi(1) \rangle_0 = -i\Delta^-(1,2), \\ \langle \psi_\lambda(1) \psi^*(2) \rangle_0 = i\Delta_\lambda^+(1,2), \end{aligned} \quad (11)$$

where

$$\Delta_\lambda^+ = \frac{\partial \Delta^+}{\partial x_\lambda} \quad \text{etc.} \quad (11)$$

and taking the definition of the causal function Δ^c from (I, (9)), we get for (10)

$$\frac{1}{16} (\Delta_\lambda^c(1,2) \Delta_\mu^c(2,4) \Delta_\nu^c(1,3) \Delta_\pi^c(3,4) + \dots)$$

which, by interchanging the variables 1, ..., 4, reduces to a single term

$$\frac{1}{16} \Delta_\lambda^c(1,2) \Delta_\mu^c(2,3) \Delta_\nu^c(3,4) \Delta_\pi^c(4,1). \quad (12)$$

We introduce now some abbreviating symbols as follows

$$\begin{aligned} (\lambda, \mu, \nu, \pi) = \Delta_\lambda^c(1,2) \Delta_\mu^c(2,3) \Delta_\nu^c(3,4) \Delta_\pi^c(4,1), \\ (\lambda, \mu, \nu) = \Delta_\lambda^c(1,2) \Delta_\mu^c(2,3) \Delta_\nu^c(3,1), \end{aligned}$$

two indices or a hyphen instead of one index shall denote respectively the corresponding second derivative of Δ^c or the function Δ^c itself.

Transforming the other terms in (9) in a similar way and using the following formulae

$$\Delta_{\mu\nu}^c(1,2) = \begin{cases} 2i\Delta_{\mu\nu}^+(1,2) - 2i\delta^{(4)}(1,2)\delta_{\mu 4}\delta_{\nu 4} & \text{for } t_1 > t_2 \\ -2i\Delta_{\mu\nu}^-(1,2) - 2i\delta^{(4)}(1,2)\delta_{\mu 4}\delta_{\nu 4} & \text{for } t_1 < t_2, \end{cases} \quad (13)$$

we get 16 terms the fourfold integrals of which, as indicated in (8), yield

$$\begin{aligned} & \frac{e^4}{64} \int d^4x_1 d^4x_2 d^4x_3 d^4x_4 A_\lambda(1) A_\mu(2) A_\nu(3) A_\pi(4) \\ & \{(\lambda, \mu, \nu, \pi) - (\lambda, \mu, \nu, \pi, -) - (\lambda, \mu, \nu, -, \pi) + (\lambda, \mu, \nu, \pi, -) \\ & - (\lambda, \mu, -, \nu, \pi) + (\lambda, \mu, -, \nu, \pi, -) + (\lambda, \mu, \nu, -, \pi) - (\lambda, \mu, \nu, \pi, -) \\ & - (-, \mu, \nu, \pi, \lambda) + (-, \mu, \nu, \pi, \lambda) + (-, \mu, \nu, -, \pi, \lambda) - (-, \mu, \nu, \pi, \lambda) \\ & + (\mu, -, \nu, \pi, \lambda) - (\mu, -, \nu, \pi, \lambda) - (\mu, \nu, -, \pi, \lambda) + (\mu, \nu, \pi, \lambda)\}, \end{aligned} \quad (14)$$

and, moreover, a sum of threefold and twofold integrals, since we may integrate the remaining terms due to the appearance of the $\delta^{(4)}$ functions in (13)

$$\begin{aligned} & -\frac{ie^4}{8} \int d^4x_2 d^4x_3 A_\lambda(1) A_\mu(2) A_4(3) A_4(3) \{(\lambda, \mu, -) - (-, \mu, \lambda) - \\ & \quad - (\lambda, \mu, -, -) + (\mu, -, \lambda)\} \\ & -\frac{e^4}{8} \int d^4x_1 d^4x_2 A_i(1) A_i(1) A_j(2) A_j(2) \Delta^c(1,2) \Delta^c(2,1). \end{aligned} \quad (15)$$

Now we have to calculate the second term in (8)

$$\begin{aligned} & \langle P(s_\lambda(1) s_\mu(2) \psi^*(3) \psi(3)) \rangle_0 = \\ & = \langle (\psi_\lambda^*(1) \psi(1) - \psi_\lambda(1) \psi^*(1)) (\psi_\mu^*(2) \psi(2) - \psi_\mu(2) \psi^*(2)) \psi^*(3) \psi(3) \rangle_0. \end{aligned}$$

In the same way as before we get the expectation value of the second term in (7) as follows

$$\begin{aligned} & -\frac{ie^4}{8} \int d^4x_1 d^4x_2 d^4x_3 A_\lambda(1) A_\mu(2) A_i(3) A_i(3) \{(\lambda, \mu, -) + (\mu, -, \lambda) - \\ & \quad - (-, \mu, \lambda) - (\lambda, \mu, -, -)\} \\ & -\frac{e^4}{4} \int d^4x_1 d^4x_2 A_4(1) A_4(1) A_i(2) A_i(2) \Delta^c(1,2) \Delta^c(2,1); \end{aligned} \quad (16)$$

the twofold integral occurs due to (13).

Finally the calculation of the vacuum expectation value of the third term in (7) gives the twofold integral

$$-\frac{e^4}{8} \int d^4 x_1 d^4 x_2 A_t(1) A_t(1) A_j(2) A_j(2) \Delta^c(1,2) \Delta^c(2,1). \quad (17)$$

The sum of (14)–(17) yields the following invariant expression for the matrix R

$$\begin{aligned} R = & \frac{e^4}{64} \int d^4 x_1 d^4 x_2 d^4 x_3 d^4 x_4 A_\lambda(1) A_\mu(2) A_\nu(3) A_\pi(4) \\ & \cdot \{ (\lambda, \mu, \nu, \pi) - (\lambda, \mu, \nu, \pi, -) - (\lambda, \mu, \nu, -, \pi) + (\lambda, \mu, \nu, \pi, -) \\ & - (\lambda, \mu, -, \nu, \pi) + (\lambda, \mu, -, \nu, \pi, -) + (\lambda, \mu, \nu, -, \pi) - (\lambda, \mu, \nu, \pi, -) \\ & - (-, \mu, \nu, \pi, \lambda) + (-, \mu, \nu, \pi, \lambda) + (-, \mu, \nu, -\pi, \lambda) - (-, \mu, \nu, \pi, \lambda) \\ & + (\mu, -, \nu, \pi, \lambda) - (\mu, -, \nu, \pi, \lambda) - (\mu, \nu, -, \pi, \lambda) + (\mu, \nu, \pi, \lambda) \}, \\ & - \frac{ie^4}{8} \int d^4 x_1 d^4 x_2 d^4 x_3 A_\lambda(1) A_\mu(2) A_\nu(3) A_\nu(3) \{ (\lambda, \mu, -) \\ & - (-, \mu, \lambda) - (\lambda, \mu, -, -) + (\mu, -, \lambda) \\ & - \frac{e^4}{8} \int d^4 x_1 d^4 x_2 A_\lambda(1) A_\lambda(1) A_\mu(2) A_\mu(2) \Delta^c(1,2) \Delta^c(2,1). \end{aligned} \quad (18)$$

In order to evaluate $R(k_1, k_2, k_3, k_4)$ we assume $A_\lambda(1) \dots A_\pi(4)$ to be plane waves:

$$A_\lambda(1) = A_{\lambda k_1} e^{ik_1^\sigma x_1^\sigma}, \quad A_\mu(2) = A_{\mu k_2} e^{ik_2^\sigma x_2^\sigma} \text{ etc.} \quad (19)$$

and take for Δ^c the representation given in (I, (13)). We need also the following integrals along the path C (see I)

$$\begin{aligned} \int_C \frac{d^4 p}{(p_\sigma^2 + 1)^2} &= \pi^2 i \int_1^\infty \frac{du}{u} - 2\pi^2 i \\ \int_C \frac{p_\sigma^2 d^4 p}{(p_\sigma^2 + 1)^3} &= \pi^2 i \int_1^\infty \frac{du}{u} - \frac{5\pi^2 i}{2}, \quad \int_C \frac{d^4 p}{(p_\sigma^2 + 1)^3} = \frac{\pi^2 i}{2} \\ \int_C \frac{p_\sigma^4 d^4 p}{(p_\sigma^2 + 1)^4} &= 8 \int_C \frac{p_1^4 d^4 p}{(p_\sigma^2 + 1)^4} = \dots = 24 \int_C \frac{p_1^2 p_2^2 d^4 p}{(p_\sigma^2 + 1)^4} = \dots = \pi^2 i \int_1^\infty \frac{du}{u} - \frac{17\pi^2 i}{6} \\ \int_C \frac{p_\sigma^2 d^4 p}{(p_\sigma^2 + 1)^4} &= 4 \int_C \frac{p_1^2 d^4 p}{(p_\sigma^2 + 1)^4} = \dots = 4 \int_C \frac{p_0^2 d^4 p}{(p_\sigma^2 + 1)^4} = \frac{\pi^2 i}{3} \\ \int_C \frac{d^4 p}{(p_\sigma^2 + 1)^4} &= \frac{\pi^2 i}{6}. \end{aligned} \quad (20)$$

After a rather long computation all the logarithmically divergent integrals cancel out, so that we obtain the finite result

$$\begin{aligned}
 R = & e^4 \pi^2 i \delta(k_1^\sigma + k_2^\sigma - k_3^\sigma - k_4^\sigma) \{ 2A_{\lambda k_1} A_{\lambda k_2} A_{\mu k_3}^* A_{\mu k_4}^* \\
 & + A_{\lambda k_1} A_{\mu k_2} A_{\nu k_3}^* A_{\nu k_4}^* [48H_{\lambda\mu} + 72K_{\lambda\mu} + 6(5k_3^2 - 2k_2^2) L_\mu \\
 & + 4(k_1^2 k_2^\mu - k_2^2(k_1^\mu + k_2^\mu) - k_3^2(k_1^\mu - k_2^\mu + k_3^\mu)) M] \\
 & + A_{\lambda k_1} A_{\mu k_2} A_{\nu k_3}^* A_{\pi k_4}^* [32N_{\lambda\mu\nu\pi} + (20k_3^2 - 8k_2^2) S_{\mu\nu\pi} \\
 & + 8(-k_1^2 k_1^\mu + k_2^2(k_1^\mu - 3k_2^\mu + 2k_3^\mu) + k_3^2(k_1^\mu - k_2^\mu + k_3^\mu)) T_{\nu\pi} \\
 & + 2((2k_1^2 + k_2^2)(-k_2^\mu + k_3^\mu)(k_1^\nu - k_2^\nu + k_3^\nu) - k_1^2 k_2^\mu (k_3^\nu - 2k_2^\nu)) U_\pi \\
 & + 2k_1^2 k_2^\mu (k_3^\nu - 2k_2^\nu)(k_1^\pi - k_2^\pi + k_3^\pi) V] + (k_3 \text{ replaced by } k_4 \text{ and vice versa}) \\
 & + (k_3 \text{ replaced by } -k_2 \text{ and vice versa}) \},
 \end{aligned} \quad (21)$$

where

$$\begin{aligned}
 H_{\mu\nu} &= \int_0^1 dx \int_0^x dy \frac{k_1^2 k_1^\mu (2y-1) + k_1^2 k_2^\mu (2y^2 - 2xy - y - 1) + k_2^2 k_1^\mu (y-x)(2y-2x-1)}{m^2 + k_1^\sigma k_2^\sigma y} \\
 K_{\lambda\mu} &= \int_0^1 du \int_0^{1-u} dv \int_v^{1-u} dw \frac{Q^\lambda Q^\mu}{P - Q^2} & P &= m^2 - 2k_2^\sigma k_3^\sigma u \\
 & & Q^\lambda &= k_1^\lambda u + k_3^\lambda v - k_2^\lambda w \\
 L_\lambda &= \int du \int dv \int dw \frac{Q^\lambda}{P - Q^2} \\
 M &= \int du \int dv \int dw \frac{1}{P - Q^2} \\
 N_{\lambda\mu\nu\pi} &= \int du \int dv \int dw \frac{Q^\lambda Q^\mu Q^\nu Q^\pi}{(P - Q^2)^2} \\
 S_{\lambda\mu\nu} &= \int du \int dv \int dw \frac{Q^\lambda Q^\mu Q^\nu}{(P - Q^2)^2} \\
 T_{\lambda\mu} &= \int du \int dv \int dw \frac{Q^\lambda Q^\mu}{(P - Q^2)^2} \\
 U_\lambda &= \int du \int dv \int dw \frac{Q^\lambda}{(P - Q^2)^2} \\
 V &= \int du \int dv \int dw \frac{1}{(P - Q^2)^2}.
 \end{aligned}$$

The integrals given here may be performed numerically for given wave vectors $k_1^2, k_2^2, k_3^2, k_4^2$ of the photons. The delta function appearing in (21) expresses the laws of conservation of energy and momentum.

For small values of k_1^2, k_2^2 we get the simple formula

$$R = 2e^4 \pi^2 i A_{\lambda k_1} A_{\lambda k_2} A_{\mu k_3} A_{\mu k_4} \delta(k_1^\sigma + k_2^\sigma - k_3^\sigma - k_4^\sigma).$$

In this case the scattering is isotropic and does not depend upon the mass constant of virtually created and annihilated mesons.

SOLUTION OF THOMAS-FERMI EQUATION FOR MOLECULES WITH AXIAL SYMMETRY

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The present paper gives analytic solutions of the Thomas-Fermi equation for neutral molecules with axial symmetry at distances very large or very small compared with the intervals between the nuclei. In the intermediate region these solutions can be combined using an interpolation with polynomials. Such an interpolation admits a determination of constants in the far solution from the boundary conditions. The solution at large distances from the nuclei is a superposition of the solution for spherical symmetry and a corrective term in the form of a development into Legendre spherical functions. Calculations have been carried out for the case of molecules consisting of two identical atoms.

1. Introduction and Formulation of the Problem

This paper, whose theme was suggested to me in Autumn 1949 by Dr. R. S. Ingarden, is an attempt at an approximate solution of the Thomas-Fermi equation in the case of axial symmetry, i. e. for molecules whose atoms are arranged in a single straight line, as for instance N_2 , CO_2 , etc. The intervals between the nuclei of the atoms, as well as the charges of the nuclei may be arbitrary, provided the differences in their magnitude are not too large. In order to simplify the calculations, we shall limit ourselves to the consideration of the case of a molecule consisting of two identical atoms. Yet it should be stressed that this means no limitation on the generality of the further development.

Analytical solutions for an atom and an ion with spherical symmetry have been given by Sommerfeld (1932 a, 1932 b) and the numerical ones by Fermi (1928), Miranda (1934) and Baker (1930). For a molecule consisting of two identical atoms a graphical-tabular solution has been given by Hund (1932). (See also Gombàs 1949).

The fundamental differential equation of the statistical theory of Thomas-Fermi has the form

$$\Delta(U - U_0) = \alpha(U - U_0)^{\frac{5}{2}} \quad \text{for } U > U_0 \quad (1)$$

where a denotes a constant >0 , U — the electric potential, and U_0 — the value of the potential at the boundary of the molecule.

This equation has been improved by Amaldi and Dirac; however, within the limits of our approximation it will do to restrict ourselves, to the investigation of the unimproved equation.

The boundary conditions are the following: (a) Conditions at infinity (i. e. the molecule encloses the whole space)

$$\lim_{r \rightarrow \infty} U = \lim_{r \rightarrow \infty} \frac{dU}{dr} = 0, \quad (2)$$

r is the distance from the centre of the molecule. The potential and the electrostatic field disappear, which involves the disappearance of U_0 . (b) in the neighbourhood of the atomic nuclei both the potential and the field must behave like Coulomb's fields, that is:

$$\begin{aligned} \lim_{r \rightarrow 0} rU &= Ze & \lim_{s \rightarrow 0} sU &= Ze \\ \lim_{r \rightarrow 0} r^2 \frac{dU}{dr} &= -Ze & \lim_{s \rightarrow 0} s^2 \frac{dU}{ds} &= -Ze \end{aligned} \quad (3)$$

where r and s are the distances from nucleus 1 and 2 respectively.

Now we shall split our problem into three parts:

1. Finding the solution for $r \gg l$
 2. Finding the solution for $r \approx l$
 3. Finding the solution for $r \ll l$.
- where l is the interval
between the nuclei

Ad 1. It is assumed that when r increases, our solution passes asymptotically into a spherical solution, and consequently the perturbation caused by axial symmetry diminishes to zero. We may assume that this perturbation is small compared with the spherical solution for the nucleus of charge $2Ze$. Of course, if the interval between the nuclei l tends to zero, then the axial-symmetrical correction must also tend to zero, which means that the constants in the terms of the correction must be functions of l .

We introduce a new variable $U = 2ZeV$, owing to which the Thomas-Fermi equation takes the form

$$\Delta V = \gamma_1 V^{\frac{3}{2}} \quad (4)$$

where $\gamma_1 = a\sqrt{2Ze}$. In accordance with the above assumptions we can write the solution in the form

$$V = V_0(r) + w(r, \varphi), \quad (5)$$

where $V_0(r)$ is the spherical solution, $w(r, \varphi)$ — the correction. For the spherical solution we take the expression

$$V_0 = \frac{144}{\gamma_1^2 r^2} \quad (6)$$

given by Sommerfeld (1932 b), which satisfies the equation as well as the conditions at infinity, but does not satisfy the conditions in the neighbourhood of the nuclei. It yields a very good approximation for r 's large with respect to l (e. g. for nitrogen ($Z=7$) for $r > 18l$). The introduction of a more accurate spherical solution of Sommerfeld does not, apart from mathematical complications, bring in any essential changes in the form of the solution.

Ad 2. Mathematically this problem is the most difficult of the three, and we shall take it up in the latter part of this paper as a problem of bridging the gap between solutions 1 and 3.

Ad 3. In this case we restrict ourselves to the neighbourhood of one of the nuclei. Of course, analogous reasoning may be applied to either of the nuclei separately.

On the basis of the results of the researches of Hund (1932), who has ascertained that in the case of a molecule consisting of two identical atoms, the solution is approximately equal to a superposition of the particular spherical solutions for each atom separately, we assume that the potential sought, has the form

$$U = ZeV_1 + ZeV_2 + Zew, \quad (7)$$

where $V_1 = V_1(r)$ is the spherical solution for atom 1, $V_2 = V_2(s)$ is the spherical solution for atom 2 and $w = w(r, \varphi)$ is the perturbation. We also assume here that the perturbation caused by the influence of the other atom, and expressed by the term $V_2 + w$ is small compared with V_1 , and vanishes together with the derivative with respect to r at $r = 0$.

For V_1 we take the solution in the form of Miranda's development (1934), whose accuracy is estimated to be of the order 10^{-6} . This solution satisfies the boundary condition at $r = 0$, and is convergent for very small r (e. g. for nitrogen $r < 0,23l$).

For V_2 we take the spherical solution of Sommerfeld (1932 b)

$$V_2(s) = \frac{1}{s} (1 + \beta_0 s^{\lambda_2})^{-\frac{\lambda_1}{2}} \quad (8)$$

where $\beta_0, \lambda_1, \lambda_2$ denote positive constants. This solution still yields a good approximation at the distance l , for elements heavier than nitrogen (e. g. for N for $r \geq 1,15l$).

While the solution for large r is of great physical importance, this is not true of the solution for small r 's has which no practical physical meaning, since the statistical theory is not applicable to descriptions of the internal atomic processes. Yet this solution is indispensable for us, since it will admit of a determination of constants appearing in the terms of perturbation in the solution for large r .

2. The Solution

(a) *for large r .* We assume that

$$w(r, \varphi) = \sum_i R_i F_i \quad (9)$$

where $R_i = R_i(r)$, $F_i = F_i(\varphi)$. R_i must vanish more strongly at infinity than r^{-4} .

If we take into consideration the inequality

$$|V_0(r)| \gg |w(r, \varphi)| \quad (10)$$

as well as the fact that V_0 satisfies the Thomas-Fermi equation in the case of spherical symmetry, then

$$\Delta V_0 + \Delta \sum_i R_i F_i = \gamma_1 (V_0 + \sum_i R_i F_i)^{\frac{3}{2}} \quad (11)$$

on developing the brackets according to the binomial formula of Newton and neglecting the higher terms, will read

$$\Delta \sum_i R_i F_i = \frac{3}{2} \gamma_1 V_0^{\frac{1}{2}} \sum_i R_i F_i, \quad V_0^{\frac{1}{2}} = \frac{12}{\gamma_1 r^2}. \quad (12)$$

A sufficient condition for the solution of this equation is that for every $i = 1, \dots, n$

$$\Delta R_i F_i = \frac{18}{r^2} R_i F_i \quad (13)$$

should be true.

(b) *for small r .* Before we pass on to the solution, we shall point out that

$$V_2 = \frac{1}{s(1 + \beta_0 s^2)^{\frac{\lambda_1}{2}}} \quad (14)$$

can be developed in a power-series with respect to r , since

$$s^2 = r^2 + l^2 - 2rl \cos \varphi \quad \text{and} \quad r < s, l. \quad (15)$$

The Thomas-Fermi equation reads

$$\Delta(V_1 + V_2 + w) = \gamma_0(V_1 + V_2 + w)^{\frac{3}{2}} \quad (16)$$

where $\gamma_0 = \alpha\sqrt{Ze}$. Denoting $V_2 + w = v$ we assume that this expression can be represented in the form of the series

$$\sum_i R_i(r) F_i(\varphi). \quad (17)$$

In a similar way we obtain the equation of the form

$$\Delta v = \frac{3}{2}\gamma_0 V_1^{\frac{3}{2}} v \quad (18)$$

where V_1 denotes Miranda's solution for spherical symmetry.

(c) for large and small r . In both cases we look for a solution for

$$\Delta R(r) F(\varphi) = \frac{3}{2}\gamma_i V_j^{\frac{3}{2}}(r) R(r) F(\varphi) \quad (19)$$

where $i, j = 0, 1$ and $i \neq j$. Carrying out the separation of variables we obtain two ordinary equations depending on a single parameter λ :

$$\text{for } F: F'' + \text{ctg } \varphi F' + (\lambda - 18)F = 0, \quad (20)$$

$$\text{for } R: \frac{d}{dr} \left(r^2 \frac{d}{dr} R \right) - [\lambda - 18 + f(r)]R = 0 \quad (21)$$

where $f(r) = \frac{3}{2}\gamma_i r^2 V_j^{\frac{3}{2}} (i \neq j)$.

The equation for F is the same for small as for large r 's and we shall try to solve it first.

The equation written in variables $\cos \varphi = \xi$ has the form

$$(\xi^2 - 1)\ddot{F} + 2\xi\dot{F} - (\lambda - 18)F = 0. \quad (22)$$

This equation belongs to Fuchs's class and has 3 regular singular points, viz. at $\xi = -1, +1, \infty$. Let us look for such solutions as would be regular in the interval $0 \leq |\xi| \leq 1$. They are found to be Legendre's polynomials (Courant-Hilbert 1937, p. 281, Smirnow 1949, p. 379).

In this manner we have imposed on λ the condition

$$\lambda = n(n+1) + 18, \quad (23)$$

where n is an integer or equal to zero, i.e. $\lambda \geq 18$. We shall now pass on to the solution with respect to R , and in particular for large r .

The equation

$$r^2 R'' + 2rR' - \lambda R = 0 \quad (24)$$

belongs to Fuch's class and has two regular singularities. It is a known Euler equation. Its solution is obtained immediately

$$R = C_1 r^{\frac{1}{2}(-1+\sqrt{1+4\lambda})} + C_2 r^{\frac{1}{2}(-1-\sqrt{1+4\lambda})}. \quad (25)$$

Two conditions must be fulfilled: 1) the exponent must not be complex (periodicity), and 2) it must not be larger than -4 . Writing $C_1 = 0$, and taking into account that $\lambda \geq 18$, the two conditions are satisfied.

The solution has assumed the form

$$R = C r^{\frac{1}{2}(-1-\sqrt{1+4\lambda})} \quad \lambda \geq 18. \quad (26)$$

Combining the results obtained for $F(\varphi, \lambda)$ and $R(r, \lambda)$ we can give the first terms of the development of the perturbation w

$$w = A_0 r^{-4.76} + A_1 r^{-5} \cos \varphi + A_2 r^{-5.42} \frac{1}{2}(3 \cos^2 \varphi - 1) + A_3 r^{-6} \frac{1}{2}(5 \cos^3 \varphi - 3 \cos \varphi) + \dots \quad (27)$$

In the case of a molecule consisting of two identical atoms (the case in question) the terms containing odd spherical functions must vanish because of symmetry. Thus $A_1, A_3, A_{2n+1}, \dots$ disappear

For molecules consisting of non-identical atoms, where enantiomorphic (mirror) symmetry is not present, these terms need not vanish of course.

The quantities A_i are specific electric momenta; they depend on the properties and the geometry of atoms and on their relative positions. In order to compute their numerical values, a solution in the neighbourhood of the nuclei is needed.

Of course our solution does not satisfy the boundary conditions for $r=0$ and $s=0$.

We pass on to the solution with respect to R for small r .

The equation has the form

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - [\mu + f(r)] R = 0 \quad (28)$$

where

$$f(r) = \frac{3}{2} \gamma_0 r^2 V_1^{\frac{1}{2}}; \quad \mu = \lambda - 18;$$

V_1 — Miranda's approximation in the form of the following development

$$V_1 = \frac{1}{r} - a \gamma_0^{\frac{2}{3}} + \frac{4}{3} \gamma_0 r^{\frac{1}{2}} - \frac{2}{5} a \gamma_0^{\frac{2}{3}} r^{\frac{3}{2}} + \frac{1}{3} \gamma_0^2 r^2 + \dots \quad a \sim 1.5 > 0. \quad (29)$$

For the purpose of calculation of $V_1^{\frac{1}{2}}$ we develop it by Newton's binomial formula, and restrict ourselves to the first two terms of the development, dropping the terms which are smaller than $\frac{1}{8}a^2\gamma_0^{\frac{4}{3}}r^{\frac{5}{2}}$. In order to remove the fractional powers of r , we shall introduce in the development a new variable $s=r^{\frac{1}{2}}$. With this variable and after substituting the development with respect to $V_1^{\frac{1}{2}}$ the equation assumes the form

$$s^2 R'' + 3s R' + R(g_0 + g_3 s^3 + g_5 s^5 + g_6 s^6 + g_8 s^8 + \dots) = 0 \quad (30)$$

where g_i 's are constants dependent on μ, a, γ_0 .

This is an equation with singularities at $s=0, \infty$, but it does not belong to Fuchs's class. It has a regular singularity at $s=0$ (the theorem about the poles of coefficients (Bieberbach 1930, p. 206), and therefore at least one of its fundamental solutions can be represented in the form

$$R = s^{\varrho} \sum_n^{\infty} a_n s^n. \quad (31)$$

The fundamental equation reads

$$\varrho(\varrho-1) + 3\varrho - 4\mu = 0; \quad \varrho_{1,2} = -1 \pm \sqrt{1+4\mu} = -1 \pm (1+2n) \quad (32)$$

since $\mu = n(n+1)$. Thus for ϱ we obtain integers, which means that only ϱ with a larger real part yields a solution not containing $\ln s$. Thus we take

$$\varrho = \varrho_2 = -1 + (1+2n) = 2n. \quad (33)$$

If a_0 is an arbitrary constant, the remaining constants are determined using the method of undetermined coefficients. We shall further denote a_0 by h_n — an arbitrary constant.

Thus

$$R_n = h_n r^n (1 + a_{3n} r^{\frac{3}{2}} + a_{5n} r^{\frac{5}{2}} + a_{6n} r^3 + a_{8n} r^4 + \dots). \quad (34)$$

Combining the two results obtained for $R(r, n)$ and $F(\varphi, n)$ we obtain for v

$$v = h_0 T_0 + h_1 r \cos \varphi T_1 + \frac{1}{2} h_2 r^2 (3 \cos^2 \varphi - 1) T_2 + \frac{1}{2} h_3 r^3 T_3 (5 \cos^3 \varphi - 3 \cos \varphi) + \dots \quad (35)$$

where

$$T_n = 1 + a_3(n) r^{\frac{3}{2}} + a_5(n) r^{\frac{5}{2}} + \dots$$

In the solution with respect to v appear the arbitrary constants h_n , normalizing the form of the solution. They are defined by the boundary conditions. In our case only two constants can be defined

by the condition at $r=0$. But, up to now, we have not made use of our physical — and therefore the most important — assumption, namely that the form of v is to a great extent influenced by V_2 (Hund, 1932), while w is merely a slight correction caused by the deformation of the field. This physical condition replaces our boundary conditions; it admits for a determination of further constants, by reducing w to a minimum.

Since V_2 is of the form

$$\{C_0 + C_{02}r^2 + C_{04}r^4 + \dots\} + r \cos \varphi \{C_1 + C_{12}r^2 + C_{14}r^4 + \dots\} \\ + r^2 \cos^2 \varphi \{C_2 + C_{22}r^2 + C_{24}r^4 + \dots\} + r^3 \cos^3 \varphi \{C_3 + \dots\} + \dots \quad (36)$$

so the condition for $\lim_{r \rightarrow 0} w = \lim_{r \rightarrow 0} \frac{dw}{dr} = 0$ is that $h_0 = C_0$ and $h_1 = C_1$.

Examining the convergency of the series T_w it appears, that beginning with a_3 , they are the alternating Leibniz series, and as such have the sum of the series smaller than the term a_3 (the first eight terms have been examined). Since $a_{3n} \leq \frac{2}{5}$, the first term exceeds by its value the remainder of the series. Thus writing successively $h_2 = C_2$, $h_3 = C_3$ etc. our assumption is satisfied.

Then the development with respect to v assumes the form

$$v = C_0(1 + a_{03}r^{\frac{3}{2}} + a_{05}r^{\frac{5}{2}} + a_{06}r^3 + \dots) - \frac{1}{3}C_2r^2(1 + a_{23}r^{\frac{3}{2}} + a_{25}r^{\frac{5}{2}} + a_{26}r^3 + \dots) \\ + C_1r \cos \varphi(1 + a_{13}r^{\frac{3}{2}} + \dots) - \frac{3}{5}C_3r^3 \cos \varphi(1 + a_{33}r^{\frac{3}{2}} + \dots) + \quad (37) \\ + C_2r^2 \cos^2 \varphi(1 + a_{23}r^{\frac{3}{2}} + \dots) - \dots + \dots \\ + C_3r^3 \cos^3 \varphi(1 + a_{33}r^{\frac{3}{2}} + \dots) - \dots + \dots$$

3. Final Remarks

To sum up the results obtained:

We have arrived at a solution at a large distance from the nuclei (in the interval where $\frac{144}{a^2 r^2}$ is a good approximation)

$$U_f = \frac{2Ze \cdot 144}{\gamma_1^2 r^4} + 2Ze \left(\frac{A_0}{r^{4,76}} + \frac{A_1}{r^5} \cos \varphi + \frac{1}{2} \frac{A_2}{r^{5,42}} (3 \cos^2 \varphi - 1) \right. \\ \left. + \frac{1}{2} \frac{A_3}{r^6} (5 \cos^3 \varphi - 3 \cos \varphi) + \dots \right), \quad (38)$$

as well as a solution at a small distance (where Miranda's solution is a good approximation

$$U_n = Ze(V_1 + V_2 + w) = Ze (\text{Miranda's development} \\ + C_0 T_0 - \frac{1}{3} C_2 r^2 T_2 + C_1 r \cos \varphi T_1 - \frac{3}{5} C_3 r^3 \cos \varphi T_3 \\ + \dots - + C_2 r^2 \cos^2 \varphi T_2 - + \dots - + C_3 r^3 \cos^3 \varphi T_3 - + \dots) \quad (39)$$

Now we should determine the constants in the development U_f . This is a rather difficult task, since the course of the potential in the part $r \sim l$ is unknown to us. But we shall bridge this gap by using an interpolation. That is, we shall take both the solutions, the far U_f and the near U_n at the boundaries of their validity in the direction of the negative and positive polar axes in r_f and r_n . In this direction the φ -angles of the sets $(\varphi, r)_f$ and $(\varphi, r)_n$ fall together and are equal to 0 or π .

The „bridge“ over the region between U_f and U_n is built up of a polynomial of the n -th order, whose values at the points r_f and r_n as well as the values of its derivatives of the n -th order should agree with the values of the functions U_f and U_n and their derivatives, including the n -th one, at the same points.

In this way we obtain $(2n+2)$ linear equations for $(n+1)$ A_l -values as well as for $(n+1)$ values of the coefficients of our polynomial.

For an interpolation at angles other than 0 and π , we should take for each direction two sets of linear equations, placing the origin of the set once in one nucleus, and once in the other, and then taking the mean.

To close this paper we shall give a general picture of the course of the potential. At large distances from the nuclei the solution approaches the spherical solution for an atom with nucleus of charge $2Ze$ (more generally $e \sum_n Z_n$). The larger r is, the smaller is the divergence from spherical symmetry. As we approach the nuclei the divergence increases, and there follows a deformation of the sphere into a cylinder narrowed between the nuclei. The incision becomes deeper and deeper, till at last the equipotential surface is torn in two parts, each of them surrounding one of the nuclei. These surfaces resembles spheres, a little deformed in the direction of the polar axis. This deformation of spherical symmetry is described by $(V_2 + w)$; as we approach the nuclei the correction decreases to zero. Thus the largest deviations from spherical symmetry lie in the region between V_n and V_f . In this region we have a continuous transition between spherical and bipolar symmetries. In this region we can no longer assume that the correction w is small compared with $v_1 + v_2$ or v_0 .

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OUTLINE OF A GENERAL THEORY OF ATOMIC COLLISIONS. PART I. COLLISIONS OF ONE PARTICLE WITH A SYSTEM OF PARTICLES

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An outline of the general non-relativistic theory of collisions of one particle with a system of particles is given, based on the most simple example of collisions with a hydrogen atom. The wellknown approximations follow from the general theory after introducing certain simplifications. The meaning of the phase shift for the wave function of an elastically scattered particle is extended to the case of unelastically scattered particles, and a general formula for the phase shift is deduced. In the case of large velocities of the colliding particle, the general formula for the phase shift tends to become the phase shift formula given by the Born approximation. For elastic scattering by „spherically symmetric rigid potentials“ the general phase shift formula is identical with the well-known phase shift formula for this special case. Some new procedures are given for approximate calculations of scattering processes in the case of medium velocities of the scattered particles. The main advantages of the proposed theory are summarized.

Introduction

The general problem of the collision theory in the non-relativistic approximation can be reduced to the problem of finding solutions with proper boundary conditions of the corresponding Schrödinger equation. In the course of the historical development of the collision theory, there has been little attempt to formulate a general systematic theory of collisions. Such a theory should start with the most convenient form for the solution of the Schrödinger equation, and should show how the known approximations (Born approximation, distorted wave approximation, rigid potential approximation) follow from the exact formulae when some quantities are neglected as small. It is intended here to fill this gap (Mott and Massey 1949, page 133) in the development of the collision theory, and to give an outline of a general method of solution of the Schrödinger equation which can also include radiative collisions. To simplify matters, the working of this method will be illustrated here on the example of a collision

of one particle (\mathbf{R}) with a hydrogen atom. In non-relativistic approximation this scattering process is described by a wave function $\Omega(E, \mathbf{R}, \mathbf{r})$ which is the solution of the appropriate Schrödinger equation and satisfies boundary conditions characteristic of collision problems. The wave function $\Omega(E, \mathbf{R}, \mathbf{r})$ depends upon the arguments $E, \mathbf{R}, \mathbf{r}$ which denote respectively

E — total energy of the system (\mathbf{R}, \mathbf{r}) composed of the incident particle (\mathbf{R}) and of the hydrogen atom,

\mathbf{R} — radius vector of the (\mathbf{R})-particle,

\mathbf{r} — radius vector of the hydrogen electron (\mathbf{r}).

We assume throughout this paper infinite mass of the hydrogen atom¹.

The boundary conditions prescribe the following asymptotic form for the wave function $\Omega(E, \mathbf{R}, \mathbf{r})$

$$\Omega(E, \mathbf{R}, \mathbf{r}) \xrightarrow{R \rightarrow \infty} \left(\sum + \int \right) \Omega_{n,u}^m(\mathbf{K}_n, \mathbf{R}) \chi_{n,u}^m(\mathbf{r}), \quad (1)$$

where the symbol $\left(\sum + \int \right)$ denotes summation over the discontinuous part and integration over the continuous part of the complete set of unperturbed wave functions² $\chi_{n,u}^m(\mathbf{r})$ of the atomic electron (\mathbf{r}). The functions $\Omega_{n,u}^m(\mathbf{K}_n, \mathbf{R})$ are, for $R \rightarrow \infty$, of the form

$$\Omega_{n,u}^m(\mathbf{K}_n, \mathbf{R}) \xrightarrow{R \rightarrow \infty} \delta_{n,n_0} e^{i(\mathbf{K}_n \mathbf{R})} + \frac{e^{i\mathbf{K}_n \mathbf{R}}}{R} f_{n,u}^m(\omega), \quad (1a)$$

\mathbf{K}_n here denotes the momentum vector $\mathbf{K}_n = M\mathbf{v}_n$ and $\mathbf{K}_{n_0} = \mathbf{K}$. This asymptotic form gives the angular distribution of the scattered (\mathbf{R})-particles with the help of the relation

$$I_{n,u}^m(\omega) d\omega = \frac{K_n}{K} |f_{n,u}^m(\omega)|^2 d\omega, \quad (2)$$

where $I_{n,u}^m(\omega)$ denotes the number of particles with initial velocity v scattered between the solid angles ω and $\omega + d\omega$ per unit time.

The main problem of the collision theory is, therefore, to calculate in the asymptotic region $R \rightarrow \infty$ the function $\Omega_{n,u}^m(\mathbf{K}_n, \mathbf{R})$ describing the scattered (\mathbf{R})-particle which has excited or ionized the given state n, u, m of the scattering system, in our case — of the hydrogen atom.

¹ When the mass M of particle (\mathbf{R}) is of the order of the protonic mass the reduced mass of the proton and the particle (\mathbf{R}) is to be used.

² n, u, m are the quantum numbers of the atomic electron (\mathbf{r}).

The usual procedure is to expand the wave function $\Omega(E, \mathbf{R}, \mathbf{r})$ according to the set of unperturbed wave functions $\chi_{n,u}^m(\mathbf{r})$ of the scattering system (hydrogen atom), and to evaluate $f_{n,u}^m(\omega)$ in expression (1 a) by assuming that $\Omega_{n,y}^m(\mathbf{K}_n, \mathbf{R})$ represents throughout the \mathbf{R} -space the wave function for the (\mathbf{R}) -particle which has excited or ionized the given state n, u, m of the hydrogen atom. This assumption in the calculation of collision processes is expressed by the fact that while solving certain integral equations we usually neglect under the integral sign all terms in the expansion of $\Omega(E, \mathbf{R}, \mathbf{r})$ with the exception of the first one (case of partial cross-section or Born approximation). Such a drastic approximation procedure amounts to complete omission of the „polarization effect“. By „polarization effect“ of the scattering system we mean the deformation of this system due to the collision. To see that the polarization effect is not taken into account by all the well-known approximation procedures of the collision theory (for instance, by the partial cross-section type, or by the Born approximation type), it is sufficient to observe that in the „collision region“, where the interaction potential of the incident particle (\mathbf{R}) with the scattering system is not negligibly small, the coefficients $\Omega_{1,0}^0(\mathbf{K}, \mathbf{R})$, for instance, of the expansion

$$\Omega(E, \mathbf{R}, \mathbf{r}) = \left(\sum + \int \right) \Omega_{n,u}^m(\mathbf{K}_n, \mathbf{R}) \chi_{n,u}^m(\mathbf{r}) \quad (2a)$$

do not represent elastically scattered wave functions of the (\mathbf{R}) -particle. The wave function of the scattering system in the collision region is deformed or polarized and, therefore, cannot be represented by the unperturbed ground-state eigenfunction $\chi_{1,0}^0(\mathbf{r})$ of the scattering system. Thus, in the collision region, the wave function for the total (\mathbf{R}, \mathbf{r}) -system should include all terms in expansion (2a) in order to take into full account the polarization effect. However, in this paper another method is proposed to deal with this polarization effect. This method seems to be especially useful when we do not know the mathematical form of all these terms or, at least, do not know the mathematical expressions for a sufficient number of these terms. Therefore, the use of the proposed method of calculation which include the polarization effect replaces, in the most important cases, an infinite number or, in practice, a large number of not well defined terms of expansion (2a) by only a few terms of the new, different, expansion of the function $\Omega(E, \mathbf{R}, \mathbf{r})$. These terms are usually better defined for nuclear collisions than are the terms of expansion (2a). This new expansion consists in developing the function $\Omega(E, \mathbf{R}, \mathbf{r})$ according to a properly defined

system of partial wavelets³ for particle (\mathbf{R}). As this system of partial wavelets is of a mathematical form which takes into account the spherically symmetric part of the interaction potential between the incident particle (\mathbf{R}) and the (\mathbf{r})-particle of the scattering system, the development according to this system is especially useful for „medium velocity collisions“. By this term we mean those collisions of the incident particle (\mathbf{R}) for which its velocity is of the same order of magnitude as the velocity of the scattering particle (\mathbf{r}). From the classical point of view it is obvious that in the case of medium velocity collisions the polarization effect of the scattering system is the largest. When we assume the mass M of particle (\mathbf{R}) to be of the same order of magnitude as the mass of particle (\mathbf{r}), then the colliding particle (\mathbf{R}) penetrates with medium velocity sufficiently deep into the scattering system, and remains there sufficiently long to cause a strong polarization effect. Applying the new development of the function $\Omega(E, \mathbf{R}, \mathbf{r})$ to the collision calculations, it can be proved that for „high velocity collisions“ the polarization effect is negligible, and the new expansion gives, after some simplification, the same result as the old one, i. e., the Born approximation.

The new development of the wave function $\Omega(E, \mathbf{R}, \mathbf{r})$ presents some advantages, especially when we have to deal with nuclear collisions. In this case, on account of the very short range of nuclear forces, the series expressing the function $f_{n,u}^m(\omega)$ in (1a) are quickly convergent, and very few terms are necessary in our new expansion. In connection with the above, the approximation procedures here given seem to be better adapted to the mathematical treatment of „medium velocity nuclear collisions“ than the old methods which were based on general properties of atomic structure (weak interaction between electrons) and not on properties of nuclear structure (strong interaction between nucleons). In the language of wave mechanics, Niels Bohr's main objection to the introduction of the old methods of calculation into nuclear collision problems was that the old methods start with unperturbed wave functions for (\mathbf{R}) or for (\mathbf{r}) particles, or for (\mathbf{R}) and (\mathbf{r}) particles together, and therefore neglect, in zero-order approximation, the strong interaction between the nucleons. This is permissible when the interaction is small, as in the case of collisions with atoms, but is surely incorrect in collisions of nuclei. To deal with nuclear collisions we must from the very beginning, i. e. already in forming the zero-order approximation, take into account the interaction between the particles. In this respect the approximation procedures outlined in this paper are more correct than the older ones.

³ See Appendix A.

Scattering of a particle by the hydrogen atom

The Schrödinger equation for a system (\mathbf{R}, \mathbf{r}) consisting of a hydrogen atom and an incident particle (\mathbf{R}) can be written in Hartree units in the following form

$$\left\{ \Delta_R + K^2 - 2M\varepsilon \left[\frac{1}{|\mathbf{R}-\mathbf{r}|} - \frac{1}{R} \right] + 2M \left[\frac{1}{2} \Delta_r + E - \frac{K^2}{2M} + \frac{1}{r} \right] \right\} \Omega(E, \mathbf{R}, \mathbf{r}) = 0, \quad (3)$$

where Δ_R and Δ_r are Laplacians for particle (\mathbf{R}) and the hydrogen electron (\mathbf{r}) respectively. K is the initial momentum of the incident particle (\mathbf{R}) , M — the mass of this particle, E — the total energy of the system; $\varepsilon = z$ for negative, and $\varepsilon = -z$ for positive charge of the (\mathbf{R}) -particle.

We assume an approximate solution of (3) in the form

$$\Phi(E, \mathbf{R}, \mathbf{r}) = \sqrt{\frac{\pi}{2}} \frac{1}{KR} \sum_{s=1}^{\infty} (2s+1) i^s F_s(K, R, r) P_s(\cos \theta_R) e^{i\sigma_s(K, r)} \varphi_s(\mathbf{r}) \quad (3a)$$

and introduce the definition $\Psi_s(K, \mathbf{r}) = e^{i\sigma_s(K, r)} \varphi_s(\mathbf{r})$, where $\Psi_s(K, \mathbf{r})$ are the functions which can be considered as coefficients in the expansion of $\Phi(E, \mathbf{R}, \mathbf{r})$ according to the orthogonal system of functions $\Phi_s(K, \mathbf{R}, r)$ given by

$$\Phi_s(K, \mathbf{R}, r) = \sqrt{\frac{\pi}{2}} \frac{1}{KR} (2s+1) i^s F_s(K, R, r) P_s(\cos \theta_R). \quad (4)$$

The functions $\Phi_s(K, \mathbf{R}, r)$ are the products of spherical harmonics, functions of the angular coordinates of particle (\mathbf{R}) and of the functions $F_s(K, R, r)$ defined by the following relations

$$\left[\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} + K^2 - 2M\varepsilon V_0(R, r) - \frac{s(s+1)}{R^2} \right] \frac{1}{KR} F_s(K, R, r) = 0, \quad (4a)$$

where:

$$V_0(R, r) = \begin{cases} \frac{1}{r} - \frac{1}{R} & \text{for } R \leq r \\ 0 & \text{for } R \geq r. \end{cases} \quad (5)$$

The potential $V_0(R, r)$ is the first term of the expansion of the potential $\frac{1}{|\mathbf{R}-\mathbf{r}|} - \frac{1}{R}$ in terms of spherical harmonics.

Boundary conditions for the functions $^4 F_s(K, R, r)$ are

$$F_s(K, R, r) \rightarrow 0 \quad \text{for } R \rightarrow 0 \quad (6)$$

$$F_s(K, R, r) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{2}{\pi}} N_s(K, r) \left[\cos \left(KR - \frac{2(s + \frac{1}{2}) + 1}{4} \pi \right) + \omega_s(K, r) e^{i \left(KR - \frac{2(s + \frac{1}{2}) + 1}{4} \pi \right)} \right] = \sqrt{\frac{2}{\pi}} \sin \left\{ KR - \frac{1}{2} \pi s + \sigma_s(K, r) \right\}, \quad (7)$$

where $\sigma_s(K, r)$ play the role of phase shifts.

The factors $N_s(K, r)$ in expression (7) are defined by the normalizing conditions

$$\int_{K - \frac{\Delta}{2}}^{K + \frac{\Delta}{2}} dt \int_0^\infty F_s(t, R, r) F_s(K, R, r) dR = 1. \quad (8)$$

The functions $F_s(K, R, r)$ are real (see Appendix A).

From formulae (4a), (5), (7) and (8) we get

$$N_s(K, r) = e^{-i\sigma_s(K, r)}, \quad (9)$$

where

$$\begin{aligned} \sigma_s(K, r) &= \arcsin \frac{-i\omega_s(K, r)}{\sqrt{1 + 2\omega_s(K, r)}} \\ \sigma_s(K, r) &= \arccos \frac{1 + \omega_s(K, r)}{\sqrt{1 + 2\omega_s(K, r)}}. \end{aligned} \quad (10)$$

The coefficients of scattering are given by 5

$$\omega_s(K, r) = \frac{-W_R \{ \sqrt{KR} I_{s+\frac{1}{2}}(KR), KR f_s(K, R, r) \}}{W_R \{ \sqrt{KR} H_{s+\frac{1}{2}}^{(1)}(KR), KR f_s(K, R, r) \}} \Big|_{R=r} \quad (11)$$

The symbols $W_R \{ \sqrt{KR} I_{s+\frac{1}{2}}, KR f_s \}$ denote the Wronskians of the functions $\sqrt{KR} I_{s+\frac{1}{2}}(KR)$ and $KR f_s(K, R, r)$ with respect to R . The functions $\sqrt{KR} I_{s+\frac{1}{2}}(KR)$ and $KR f_s(K, R, r)$ are regular solutions of the following equations

$$\begin{aligned} L_1 \sqrt{KR} \begin{Bmatrix} I_{s+\frac{1}{2}}(KR) \\ H_{s+\frac{1}{2}}^{(1)}(KR) \end{Bmatrix} &\equiv \left[\frac{d^2}{dR^2} - \frac{s(s+1)}{R^2} \right] \sqrt{KR} \begin{Bmatrix} I_{s+\frac{1}{2}}(KR) \\ H_{s+\frac{1}{2}}^{(1)}(KR) \end{Bmatrix} \\ &= -K^2 \sqrt{KR} \begin{Bmatrix} I_{s+\frac{1}{2}}(KR) \\ H_{s+\frac{1}{2}}^{(1)}(KR) \end{Bmatrix}, \end{aligned} \quad (12)$$

$$\begin{aligned} L_2 KR f_s(K, R, r) &\equiv \left[\frac{d^2}{dR^2} - 2M\varepsilon V_0(R, r) - \frac{s(s+1)}{R^2} \right] KR f_s(K, R, r) \\ &= -K^2 KR f_s(K, R, r). \end{aligned} \quad (13)$$

⁴ Appendix A. Formulae (A. 11) and (A. 14).

⁵ Appendix A. Formula (A. 18).

$W_R\{\sqrt{KR}H_{s+1/2}^{(1)}, KRf_s\}$ in the denominator of (11) denotes the Wronskian of the outgoing solution of equation (12) and the regular solution of equation (13). Both Wronskians in (11) are taken for $R=r$.

Insert expression (2) into equation (1), and use the expansion

$$\begin{aligned} \frac{1}{|R-r|} &= \sum_{j=0}^{\infty} \left[\frac{R}{r} \right]^j P_j(\cos \theta_{R,r}) \\ &= \sum_{j=0}^{\infty} \left[\frac{R}{r} \right]^j \sum_{m=-j}^{m=+j} \frac{(j-|m|)!}{(j+|m|)!} P_j^{|m|}(\cos \theta_R) P_j^{|m|}(\cos \theta_r) e^{im(\varphi_R - \varphi_r)}, \end{aligned} \quad (14)$$

where the symbols $\left[\frac{R}{r} \right]^j$ denote functions defined by

$$\left[\frac{R}{r} \right]^j = \begin{cases} \frac{1}{r} \left(\frac{R}{r} \right)^j & \text{for } R < r \\ \frac{1}{R} \left(\frac{r}{R} \right)^j & \text{for } R > r. \end{cases} \quad (15)$$

Then

$$\begin{aligned} &\sum_{s=0}^{\infty} i^s (2s+1) \Psi_s(\mathbf{r}) P_s(\cos \theta_R) \left[\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} + K^2 \right. \\ &\quad \left. - 2M\varepsilon V_0(R, r) - \frac{s(s+1)}{R^2} \right] F_s(K, R, r) \frac{1}{KR} \\ &- \frac{2M\varepsilon}{KR} \sum_{s=0}^{\infty} (2s+1) i^s \Psi_s(\mathbf{r}) F_s(K, R, r) P_s(\cos \theta_R) \sum_{j=1}^{\infty} \left[\frac{R}{r} \right]^j P_j(\cos \theta_{R,r}) \\ &= -\frac{M}{KR} \sum_{s=0}^{\infty} (2s+1) i^s P_s(\cos \theta_R) \left\{ F_s(K, R, r) \left[\Delta_r + 2 \left(E - \frac{K^2}{2M} \right) + \frac{2}{r} \right] \Psi_s(\mathbf{r}) \right. \\ &\quad \left. + \Psi_s(\mathbf{r}) \left\{ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right\} F_s(K, R, r) + 2\nabla_r \Psi_s(\mathbf{r}) \frac{\partial}{\partial r} F_s(K, R, r) \right\}. \end{aligned} \quad (16)$$

All the terms of the first sum on the left-hand side of equation (16) vanish on account of equation (4a). Multiplied on the left by $F_l(K, R, r) P_l(\cos \theta_R)$ and integrated over the interior of a sphere of radius Z , equation (16) gives, on account of the orthogonality of the Legendre polynomials, the following system of equations

$$\begin{aligned} A_{ll}(K, Z, r) \left[\Delta_r + 2 \left(E - \frac{K^2}{2M} \right) + \frac{2}{r} \right] \Psi_l(\mathbf{r}) &= -B_{ll}(K, Z, r) \Psi_l(\mathbf{r}) \\ &\quad - \frac{2}{r} C_{ll}(K, Z, r) \Psi_l(\mathbf{r}) - 2C_{ll}(K, Z, r) \nabla_r \Psi_l(\mathbf{r}) \\ &+ \sum_{j=1}^{\infty} \sum_{\substack{|l+j| \geq s \\ |l-j| \leq r}} (2s+1) i^{s-l} P_l(\cos \theta_R) \int_{-1}^{+1} P_j P_s P_l d \cos \theta_R D_{l,s}^l(K, Z, r) \Psi_s(\mathbf{r}), \end{aligned} \quad (17)$$

where

$$\begin{aligned}
 A_{ll}(K, Z, r) &= \int_0^Z \{F_l(K, R, r)\}^2 dR, \\
 B_{ll}(K, Z, r) &= \int_0^Z F_l(K, R, r) \frac{\partial^2}{\partial r^2} F_l(K, R, r) dR, \\
 C_{ll}(K, Z, r) &= \int_0^Z F_l(K, R, r) \frac{\partial}{\partial r} F_l(K, R, r) dR, \\
 D_{l,s}^j(K, Z, r) &= \int_0^Z F_l(K, R, r) \left[\frac{R}{r} \right] F_s(K, R, r) dR.
 \end{aligned} \tag{18}$$

Evaluating the limits (see Appendix B)

$$\begin{aligned}
 \lim_{z \rightarrow \infty} \frac{B_{ll}(K, Z, r)}{A_{ll}(K, Z, r)} &\rightarrow -U_{ll}(K, r) = -\frac{1}{v^2} \left\{ \frac{\pi \varepsilon}{r^2} \int_0^r [F_l(K, R, r)]^2 dR \right\}^2, \\
 \lim_{z \rightarrow \infty} \frac{C_{ll}(K, Z, r)}{A_{ll}(K, Z, r)} &\rightarrow V_{ll}(K, r) = 0, \\
 \lim_{z \rightarrow \infty} \frac{D_{l,s}^j(K, Z, r)}{A_{ll}(K, Z, r)} &\rightarrow U_{l,s}^j(K, r) = 0,
 \end{aligned} \tag{19}$$

we obtain finally equations (17) in the form

$$\left[\Delta_r + 2 \left(E - \frac{K^2}{2M} \right) + \frac{2}{r} \right] \Psi_l(\mathbf{r}) = U_{ll}(K, r) \Psi_l(\mathbf{r}). \tag{20}$$

The system of equations (19) can be solved in spherical coordinates. Putting

$$\Psi_l(\mathbf{r}) = g_{l,u_0}(r) P_{u_0}^{|m_0|}(\cos \theta_r) e^{im_0 \varphi_r}, \tag{21}$$

we get

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + 2 \left(E - \frac{K^2}{2M} \right) + \frac{2}{r} - \frac{u_0(u_0+1)}{r^2} \right] g_{l,u_0}(r) = U_{ll}(K, r) g_{l,u_0}(r). \tag{22}$$

The approximate solution of (22) may be found by special assumptions concerning the velocity v and mass M of the incident particle. We here assume that the system (22) is solved and that the functions $\Psi_s(\mathbf{r})$ are found with the required degree of approximation. Our solution of equation (3) is determined by the given experimental conditions. These conditions suggest the following asymptotic form of this solution

$$\Phi(E, \mathbf{R}, \mathbf{r}) \rightarrow \sum_{l=0}^{\infty} \left(\sum + \int \right) X_{n,l}^{u,m}(\mathbf{R}) \chi_{n,l}^m(\mathbf{r}), \tag{23}$$

where

$$X_{n,l}^{u,m}(\mathbf{R}) = h_{n,l}^u(K_n, R) P_l^{[m]}(\cos \theta_R) e^{im\varphi_R}, \quad (24)$$

$$\chi_{n,u}^m(\mathbf{r}) = y_{n,u}(\xi_n, r) P_u^{[m]}(\cos \theta_r) e^{im\varphi_r}, \quad (25)$$

$$E = \frac{K^2}{2M} + \xi_n, \quad E = \frac{K_n^2}{2M} + \xi_n, \quad \mathbf{s}_0 + \mathbf{u}_0 = \mathbf{l} + \mathbf{u}. \quad (25a)$$

The asymptotic form (23) expresses the fact that in all experimental arrangements the scattering particle (\mathbf{R}) is observed at a great distance $R \rightarrow \infty$ from the collision center (hydrogen nucleus). For these large distances the interaction between the incident particle (\mathbf{R}) and the hydrogen atom is sufficiently small to be neglected. Thus, the situation observed experimentally can be described by the sum of products of non-perturbed atomic wave functions $\chi_{n,u}^m(\mathbf{r})$ for the electron and wave functions $X_{n,l}^{u,m}(\mathbf{R})$ for the scattered particle. The functions $X_{n,l}^{u,m}(\mathbf{R})$ correspond to the given excitation of the state (n, u, m) of the atom. The sign ($\sum + \int$) has the same meaning as in (1). The functions $\chi_{n,u}^m(\mathbf{r})$ are described in a unique manner by the main, the orbital, and the magnetic quantum numbers n, u and m , respectively. Equations (25a) express the conservation laws of energy and angular momentum for our (\mathbf{R}, \mathbf{r})-system. $\mathbf{s}_0, \mathbf{l}, \mathbf{u}_0, \mathbf{u}$ denote the initial and final values of the angular momentum vectors for the (\mathbf{R}) and (\mathbf{r}) particles, respectively. The asymptotic form (23) of our solution (2) must be consistent with these conservation laws. That this is really the case can be seen immediately for the energy conservation law from definitions (24) and (25); the angular momentum conservation law may readily be inferred from the phase shift formula which will be deduced presently. Multiplying equation (3) on the left by $\chi_{n,u}^{*m}(\mathbf{r})$, and integrating over the space \mathbf{r} , we obtain

$$\begin{aligned} \{A_R + 2M(E - \xi_n)\} \int \chi_{n,u}^{*m}(\mathbf{r}) \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r + 2M \int \chi_{n,u}^{*m}(\mathbf{r}) \left\{ \frac{1}{2} A_r + \xi_n \right. \\ \left. + \frac{1}{r} \right\} \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r = 2M\varepsilon \int \chi_{n,u}^{*m}(\mathbf{r}) \left[\frac{1}{R-r} - \frac{1}{R} \right] \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r. \end{aligned} \quad (26)$$

In equations (25) and (26) ξ_n denotes the energy of the atomic electron in the state n, u, m , and $d\tau_r$ is the element of the r -space.

From the behaviour of the functions $\chi_{n,u}^{(m)}(\mathbf{r}), \Phi_s(\mathbf{r})$ at the origin of the coordinate system and at infinity, it is possible to show with the help of Green's theorem that ⁶

$$\begin{aligned} 2M \int \chi_{n,u}^{*m}(\mathbf{r}) \left\{ \frac{1}{2} A_r + \xi_n + \frac{1}{r} \right\} \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r \\ = 2M \int \Phi(E, \mathbf{R}, \mathbf{r}) \left\{ \frac{1}{2} A_r + \xi_n + \frac{1}{r} \right\} \chi_{n,u}^{*m}(\mathbf{r}) d\tau_r. \end{aligned} \quad (27)$$

⁶ See Appendix A.

The right-hand side of this equation vanishes, since the functions $\chi_{n,u}^{*m}(\mathbf{r})$ are non-perturbed wave-functions for the atomic electron and fulfill the Schrödinger equation for the hydrogen atom. Equation (26) then takes the form

$$\begin{aligned} & \{\Delta_R + 2M(E - \xi_n)\} \int \chi_{n,u}^{*m}(\mathbf{r}) \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r \\ &= 2M\varepsilon \int \chi_{n,u}^{*m}(\mathbf{r}) \left[\frac{1}{|\mathbf{R} - \mathbf{r}|} - \frac{1}{R} \right] \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r. \end{aligned} \quad (28)$$

With the help of relation (23) it is easy to show that for the above mentioned reason we are only interested in the asymptotic form of the solution of equation (28). For $R \rightarrow \infty$ we have

$$\int \chi_{n,u}^{*m}(\mathbf{r}) \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r \rightarrow \sum_{l=0}^{\infty} X_{n,l}^{u,m}(\mathbf{R}) \equiv \Omega_{n,u}^m(\mathbf{R}). \quad (29)$$

As a result of equation (3a), page 227, the solution of equation (28) for $R \geq r \rightarrow \infty$ has the following form

$$\begin{aligned} & \int \chi_{n,u}^{*m}(\mathbf{r}) \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r \rightarrow \delta_{nn_0} e^{iK_n R \cos \theta_R} \\ & + \sqrt{\frac{\pi}{2}} \frac{1}{KR} \sum_{l=0}^{\infty} (2l+1) i^l \sqrt{KR} H_{l+1/2}^{(1)}(KR) \times e^{i\eta_{l,n}^{u,m}} \sin \eta_{l,n}^{u,m} P_l(\cos \theta_R). \end{aligned} \quad (30)$$

Thus we have, on account of (29), (30) and (A.5) the following asymptotic expression for $\Omega_{n,u}^m$

$$\Omega_{n,u}^m(\mathbf{R}) \xrightarrow{R \rightarrow \infty} \delta_{nn_0} e^{iK_n R \cos \theta_R} + \frac{e^{iK_n R}}{R} \frac{1}{K} \sum_{l=0}^{\infty} (2l+1) e^{i\eta_{l,n}^{u,m}} \sin \eta_{l,n}^{(u,m)} P_l(\cos \theta_R). \quad (31)$$

Using the definition

$$f_{n,u}^m(\theta_R) = \frac{1}{K} \sum_{l=0}^{\infty} (2l+1) e^{i\eta_{l,n}^{u,m}} \sin \eta_{l,n}^{u,m} P_l(\cos \theta_R), \quad (32)$$

we can write expression (31) in the following form

$$\Omega_{n,u}^m(\mathbf{R}) \xrightarrow{R \rightarrow \infty} \delta_{nn_0} e^{iK_n R \cos \theta_R} + \frac{e^{iK_n R}}{R} f_{n,u}^m(\theta_R). \quad (33)$$

It is known that the required solution of equation (28) may be written

$$\int \chi_{n,u}^{*m}(\mathbf{r}) \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_r = \delta_{nn_0} e^{iK_n R \cos \theta_R} - \frac{2M\varepsilon}{4\pi} \int d\tau_r \int \frac{e^{iK_n |R-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|} \times \chi_{n,u}^{*m}(\mathbf{r}) \left[\frac{1}{|\mathbf{R}-\mathbf{r}|} - \frac{1}{R} \right] \Phi(E, \mathbf{R}, \mathbf{r}) d\tau_{R'}. \quad (34)$$

For the region $R > R'$ use the expansion

$$\frac{e^{iK_n |R-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|} = ik_n \sum_{l=0}^{\infty} (2l+1) \sqrt{\frac{\pi}{2K_n R}} H_{l+1/2}^{(1)}(K_n R) \sqrt{\frac{\pi}{2K_n R'}} I_{l+1/2}(K_n R') P_l(\cos \theta_{RR'}). \quad (35)$$

Then the general formula for the phase shift $\eta_{l,n}^{u,m}$ becomes, after comparison of equation (34) with expression (30) in the region $R \geq r \rightarrow \infty$

$$e^{i\eta_{l,n}^{u,m}} \sin \eta_{l,n}^{u,m} = -\frac{1}{K_n} \frac{2M\varepsilon}{4\pi} \int d\tau_r \int \sqrt{\frac{\pi}{2} K_n R'} I_{l+1/2}(K_n R') \left\{ \frac{1}{|\mathbf{R}'-\mathbf{r}|} - \frac{1}{R'} \right\} \chi_{n,u}^{*m}(\mathbf{r}) \times \frac{(l-|m|)!}{(l+|m|)!} K R' \Phi(E, \mathbf{R}', \mathbf{r}) (-i)^l P_l(\cos \theta_{R'}) e^{-im\varphi_{R'}} \sin \theta_{R'} d\theta_{R'} dR' d\varphi_{R'}. \quad (36)$$

The above formula may be written in the more explicit form

$$e^{i\eta_{l,n}^{u,m}} \sin \eta_{l,n}^{u,m} = -\frac{2\pi M\varepsilon}{K_n} \sum_{|u-u_0| \leq l} \sum_{|l-j| \leq s}^{|u+u_0| \geq j, |l+j| \geq s} (2s+1) (-i)^{l-s} \int_0^{\infty} y_{n,u}(r) g_{n_0,u_0}(r) \times \int_0^{\infty} \sqrt{\frac{\pi}{2} K_n R'} I_{l+1/2}(K_n R') \left\{ \left[\frac{R'}{r} \right]^j - \frac{\delta_{j0}}{R'} \right\} \sqrt{\frac{\pi}{2}} F_s(K_n, R', r) dR' r^2 dr \times \frac{(j-|m|)! (l-|m|)!}{(j+|m|)! (l+|m|)!} \int_{-1}^{+1} P_j P_l P_s d \cos \theta_{R'} \int_{-1}^{+1} P_u^{l|m|} P_j P_{u_0}^{l|m|} d \cos \theta_r. \quad (37)$$

For large velocities v of the scattered particle (\mathbf{R}) we have, due to (4), (5), (18), and (A.25), the approximate equation

$$\Phi(E, \mathbf{R}, \mathbf{r}) \sim e^{iKR \cos \theta_R} \chi_{n_0, u_0}^m. \quad (38)$$

Because of (36) the functions $f_{n,u}^m(\omega_R)$ will be approximately given by the following expressions

$$f_{n,u}^m(\omega_R) \sim \frac{-2M\varepsilon}{4\pi} \int \int e^{i(KR') - i(K_n R')} \left\{ \frac{1}{|\mathbf{R}'-\mathbf{r}|} - \frac{1}{R'} \right\} \chi_{n_0, u_0}^m(\mathbf{r}) \chi_{n,u}^{*m}(\mathbf{r}) d\tau_{R'} d\tau_r \quad (39)$$

which are identical with the formula for $f_{n,u}^m(\omega_R)$ deduced by means of the Born approximation. In the case in which the velocity v and

the energy of the scattered particle are small in comparison with the velocity and energy of the atomic electron we have almost exclusively elastic scattering. In this case we can apply the rigid potential approximation (method of partial cross-sections), assuming the wave functions $\varphi_s(\mathbf{r}), \chi_{n,u}^{*m}(\mathbf{r})$ for the electron (\mathbf{r}) to be identical with the wave function $\chi_{n_0, u_0}^m(\mathbf{r})$ for the ground state of the atom. This assumption leads to $F_s(K, R, r)$ -functions which are independent of the parameter r , and (36) becomes the well-known formula for the phase shift of the rigid potential approximation. Thus

$$\sin \eta_{l,1}^{0,0} = -\frac{1}{K} \int \sqrt{\frac{\pi K R}{2}} I_{l+1/2}(K R') U(R') \sqrt{\frac{\pi}{2}} F_l(K, R', r_0) dR', \quad (40)$$

where the potential $U(R')$ is given by

$$U(R') = 2M\varepsilon \int |\chi_{n_0, u_0}^m(\mathbf{r})|^2 \left\{ \frac{1}{|\mathbf{R}' - \mathbf{r}|} - \frac{1}{R} \right\} d\tau_r. \quad (41)$$

It is easy to give an outline of the approximation methods for collision problems on the basis of the general collision theory given above. For collisions in which the velocity of the incident particle is greater than the velocity of the particles of the scattering system, it is possible to establish a method of approximation for the computation of phase shifts for the wave function of particle (\mathbf{R}), taking advantage of the following approximate identity

$$\begin{aligned} \frac{2}{\pi_i} K R f_s(K, R, r) &\simeq \frac{1}{K} W_{R=r} \{ \sqrt{K R} H_{s+1/2}^{(1)} K R f_s \} \sqrt{K R} I_{s+1/2}(K R) \\ &- \frac{2\varepsilon}{v} \left\{ \sqrt{K R} H_{s+1/2}^{(1)}(K R) \times \int_a^R \sqrt{K R'} I_{s+1/2}(K R') V_0(R', r) K R' f_s(K, R', r) dR' \right. \\ &\quad \left. + \sqrt{K R} I_{s+1/2}(K R) \times \int_R^r \sqrt{K R'} H_{s+1/2}^{(1)}(K R') V_0(R', r) K R' f_s(K, R', r) dR' \right\}. \end{aligned} \quad (42)$$

With a proper choice of the lower limit a of the integral, the expression $\sqrt{K R} H_{s+1/2}^{(1)}(K R) \times W_{R=a} \{ \sqrt{K R} I_{s+1/2}(K R), K R f_s(K, R, r) \}$ which has been omitted in (42) represents a negligibly small quantity in comparison with the remaining terms of (42).

The identity (42) with respect to the variable R can be treated as an integral equation for the determination of the functions $K R f_s(K, R, r)$. Solving this integral equation by the iteration method of Liouville-Neumann, we get expansions of the $K R f_s(K, R, r)$ -functions in ascending powers of ε/v . The quicker these series converge, the

greater is the velocity of the incident particle (R) in comparison with the velocity of the (r)-particle of the scattering system. Using these expansions of the $KRf_s(K, R, r)$ -functions, we obtain a scheme of approximation for phase shift computation when $v > 1$.

For collisions of the „resonance type“ which can be characterized by the inequality

$$\left| K^2 - \frac{2M\varepsilon}{\bar{r}} \right| \frac{1}{2M\varepsilon} < 1. \quad (43)$$

where \bar{r} denotes the mean value of the radial coordinate of the hydrogen electron, the functions $KRf_s(K, R, r)$ satisfy the following approximate identities

$$\begin{aligned} KRf_s(K, R, r) &\simeq 2RW_{R=r} \{ \sqrt{8M\varepsilon R} H_{2s+1}^{(1)}(\sqrt{8M\varepsilon R}), KRf_s(K, R, r) \} I_{2s+1}(\sqrt{8M\varepsilon R}) \\ &- \frac{2M\varepsilon}{2M\varepsilon} \frac{r}{\sqrt{8M\varepsilon R}} \left[H_{2s+1}^{(1)}(\sqrt{8M\varepsilon R}) \int_{x_0}^x \sqrt{8M\varepsilon R'} KR'^2 f_s(K, R', r) I_{2s+1}(\sqrt{8M\varepsilon R'}) d\sqrt{8M\varepsilon R'} \right. \\ &\quad \left. + I_{2s+1}(\sqrt{8M\varepsilon R}) \int_x^{x_1} \sqrt{8M\varepsilon R'} H_{2s+1}^{(1)}(\sqrt{8M\varepsilon R'}) KR'^2 f_s(K, R', r) d\sqrt{8M\varepsilon R'} \right], \quad (44) \end{aligned}$$

where $x = \sqrt{8M\varepsilon R}$, $x_0 = \sqrt{8M\varepsilon a}$, $x_1 = \sqrt{8M\varepsilon r}$. These functions also can be found by means of the above mentioned Liouville-Neumann procedure, which in the case of „resonance collisions“ gives an expansion of the functions $KRf_s(K, R, r)$ in terms of ascending powers of $\left(K^2 - \frac{2M\varepsilon}{r} \right) / 2M\varepsilon$. By „resonance collisions“ we mean a type of collisions in which the absolute value of the energy of the scattered initial particle is of the same order of magnitude as the potential energy of the incident particle.

Using the above mentioned expansion in our general collision theory, we obtain a scheme for approximate computations of phase shifts for „resonance collisions“.

The generalization of equations (36) and (37) for phase shifts in the case of collisions with systems composed of many particles is obvious (separate coordinates for each particle of the scattering system, instead of the coordinates r, θ_r, φ_r for one electron in (3a)).

General conclusions

It is obvious from the above calculations that (3a) is only an approximate solution of the Schrödinger equation (3). It does not correspond to the given value E of the total energy of system (R, r)

(cf. equation (25a)). Inserting solution (3a) in equation (3), we get the system of equations (18), which determines the coefficients $\Psi_s(K, \mathbf{r})$ in expansion (3a). This system is fulfilled not for the energy $E - K^2/2M$ of the ground state of the atom, but for the following values of the atomic energy

$$E + \Delta_0 - \frac{K^2}{2M}, \quad E + \Delta_1 - \frac{K^2}{2M},$$

where Δ_l denotes the increase of energy of the scattering system due to its interaction with the partial streamlets (Appendix A, page 237) of (\mathbf{R}) particles, corresponding to the partial wavelets $\Phi_s(K, \mathbf{R}, r)$; Δ_l is in general small in comparison with $E - K^2/2M$. This is a consequence of the small value of the perturbing potentials $U_H(K, r)$ in the equations of definition (18).

Taking into account the equation for energy conservation

$$E = \frac{K_l^2}{2M} + \Delta_l + \xi_{n_0},$$

we can get the following form for the second approximation of the solution of equation (3)

$$\Phi(E, \mathbf{R}, \mathbf{r}) = \sqrt{\frac{\pi}{2}} \sum_{l=0}^{\infty} \frac{1}{K_l R} F_l(K_l, R, r) P_l(\cos \theta_R) (2l+1) i^l e^{i\sigma_l(K_l, r)} \varphi_l(r), \quad (45)$$

where

$$K_l = \sqrt{K^2 - 2M\Delta_l}.$$

The next approximations of type (45) gives us the sets of values $K_l^{(1)}, K_l^{(2)} \dots$, converging to limiting values \bar{K}_l . The convergence is rather quick on account of the small value of the potentials $U_H(K, r)$. The expansion of type (45), including the set of limiting values for \bar{K}_l , will be the eigensolution of equation (3) corresponding to the eigenvalue of the energy E of the whole system (\mathbf{R}, \mathbf{r}) .

In spite of frequent computation complications, the method presented here considerably increases the precision of the calculations. This is desirable especially when application of other methods is rather objectionable, as for instance for medium velocity nuclear and atomic collisions and „resonance collisions“. In all these cases the theory proposed here reaches beyond the range of known methods, establishing approximate computation procedures for the separate types of collisions. For the velocity of the incident particle (\mathbf{R}) greater than the velocity of particle (\mathbf{r}) of the scattering system, the Born approximation, for instance, constitutes the zero-order approx-

ximation of the approximation procedure which corresponds to the iteration method of Liouville-Neumann for the solution of certain integral equations.

In conclusion, the following chief advantages of the proposed theory may be stressed:

1) In comparison with variational methods (Huang 1949) the methods applied in this theory are easy to generalize to cases of collisions with many-particle scattering systems.

2) The present theory can be applied without any restriction to all cases of collisions of a particle with a system of particles.

3) With the help of the above theory, known methods of computing collision processes can be obtained as zero approximations in more precise calculations.

4) The theory gives a possibility of developing new methods of approximations.

5) The theory takes into full account the „polarization“ of the scattering system.

6) The theory allows for the collective treatment of the particles of the scattering system, and yields a possibility of taking into account the correlation of their positions.

7) Multiple simultaneous excitation or ionization of the scattering system may be computed by this theory more exactly than before.

* * *

Appendix A

The approximate solution (3a) of equation (3) represents an expansion according to the following system of functions

$$\Phi_s(K, \mathbf{R}, r) = \sqrt{\frac{\pi}{2}} (2s+1) i^s \frac{1}{KR} F_s(K, R, r) P_s(\cos \theta_R), \quad (\text{A. 1})$$

which we shall call wavelets.

The decomposition into the system of wavelets of the incident and the scattered wave functions of the incident particle (\mathbf{R}) corresponds to the decomposition into partial streamlets of the incident scattered stream of particles, each for each azimuthal quantum number s of the incident particle (\mathbf{R}). We assume that the wavelets depend parametrically on the radial coordinate r of the electron. In expansion (3a) they appear multiplied by the weight factor

$$\Psi_s(K, \mathbf{r}) = \varphi(\mathbf{r}) e^{i\sigma_s(K, r)}. \quad (\text{A. 2})$$

This statistical weight factor gives the probability that the position of the atomic electron during the collision⁷ will be present in the region specified by the electronic coordinates $\mathbf{r}, \mathbf{r} + d\mathbf{r}$. The form of the weight factor $\Psi_s(\mathbf{K}, \mathbf{r})$ depends on the deformation of the electron wave function due to collision. This deformation is different for each collision parameter $R_s^* = \sqrt{s(s+1)}/K$ (classical distance of closest approach for the free particle) of the incident particle, and is expressed by the perturbed electronic wave function, determined by the Schrödinger equation (18) together with the usual condition of boundedness.

Specifying in (3a) the values of the electronic coordinates \mathbf{r} , we have for $R \geq r$

$$\Phi(E, \mathbf{R}, \mathbf{r}) = \sqrt{\frac{\pi}{2}} \frac{1}{KR} \sum_{s=0}^{\infty} (2s+1) i^s \sqrt{KR} \{I_{s+1/2}(KR) + \omega_s(K, r) H_{s+1/2}^{(1)}(KR)\} P_s(\cos \theta_R) \varphi_s(\mathbf{r}), \quad (\text{A. 3})$$

where $I_{s+1/2}(KR)$ and $H_{s+1/2}^{(1)}(KR)$ are Bessel and Hankel functions of the first kind and order $s + \frac{1}{2}$. In (A. 3) the first part of the expression in brackets corresponds to the incident wavelet, and the second one — to the scattered wavelet with scattered intensity $\omega_s(K, r)$.

Taking into account the following asymptotic forms

$$I_{s+1/2}(KR) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{2}{\pi KR}} \cos \left(KR - \frac{2(s+\frac{1}{2})+1}{4} \pi \right) = \sqrt{\frac{2}{\pi KR}} \sin \left(KR - \frac{1}{2} \pi s \right) \quad (\text{A. 4})$$

and

$$H_{s+1/2}^{(1)}(KR) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{2}{\pi KR}} e^{i \left(KR - \frac{2(s+\frac{1}{2})-1}{4} \pi \right)} = \sqrt{\frac{2}{\pi KR}} [\sin (KR - \frac{1}{2} \pi s) - i \cos (KR - \frac{1}{2} \pi s)], \quad (\text{A. 5})$$

we have

$$\Phi(E, \mathbf{R}, \mathbf{r}) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{\pi}{2}} \frac{1}{KR} \sum_{s=0}^{\infty} (2s+1) i^s \sqrt{\frac{2}{\pi}} \{[1 + \omega_s(K, r)] \sin (KR - \frac{1}{2} \pi s) - i \omega_s(K, r) \cos (KR - \frac{1}{2} \pi s)\} P_s(\cos \theta_R) \varphi_s(\mathbf{r}) \quad (\text{A. 6})$$

$$\Phi(E, \mathbf{R}, \mathbf{r}) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{\pi}{2}} \frac{1}{KR} \sum_{s=0}^{\infty} (2s+1) i^s e^{i \sigma_s(K, r)} \varphi_s(\mathbf{r}) \sqrt{\frac{2}{\pi}} \sin \{KR - \frac{1}{2} \pi s + \sigma_s(K, r)\} P_s(\cos \theta_R) \quad (\text{A. 7})$$

⁷ The collisions are considered here as a stationary process.

where we have put

$$\cos \sigma_s(K, r) = \frac{1 + \omega_s(K, r)}{\sqrt{1 + 2\omega_s(K, r)}} \quad (\text{A. 8})$$

$$\sin \sigma_s(K, r) = \frac{-i\omega_s(K, r)}{\sqrt{1 + 2\omega_s(K, r)}}. \quad (\text{A. 9})$$

We therefore have formulae (10) for $\sigma_s(K, r)$ and the following formula

$$e^{i\sigma_s(K, r)} = \sqrt{1 + 2\omega_s(K, r)} = \frac{1}{N_s(K, r)}. \quad (\text{A. 10})$$

The functions $F_s(K, R, r)$ in (3a) can be written for $R \geq r$

$$F_s(K, R, r) = \sqrt{KR} \{I_{s+1/2}(KR) + \omega_s(K, r) H_{s+1/2}^{(1)}(KR)\} e^{-i\sigma_s(K, r)}. \quad (\text{A. 11})$$

We then have asymptotically

$$F_s(K, R, r) \xrightarrow{R \rightarrow \infty} \sqrt{\frac{2}{\pi}} \sin \{KR - \frac{1}{2}\pi s + \sigma_s(K, r)\}. \quad (\text{A. 12})$$

We have also for $R \leq r$

$$\begin{aligned} \Phi(E, \mathbf{R}, \mathbf{r}) &= \\ &= \sqrt{\frac{\pi}{2}} \frac{1}{KR} \sum_{s=0}^{\infty} (2s+1) i^s v_s(K, r) KR f_s(K, R, r) P_s(\cos \theta_R) \varphi_s(\mathbf{r}) \end{aligned} \quad (\text{A. 13})$$

and

$$\begin{aligned} F_s(K, R, r) &= v_s(K, r) KR f_s(K, R, r) e^{-i\sigma_s(K, r)} \\ &= N_s(K, r) v_s(K, r) KR f_s(K, R, r), \end{aligned} \quad (\text{A. 14})$$

where

$$\begin{aligned} f_s(K, R, r) &= \left(2 \sqrt{K^2 - \frac{2M\varepsilon}{r}} R\right)^s e^{i\sqrt{K^2 - \frac{2M\varepsilon}{r}} R} \\ &{}_1F_1\left(\frac{-Mi\varepsilon}{\sqrt{K^2 - \frac{2M\varepsilon}{r}}} + s + 1; 2s + 2, -2iR \sqrt{K^2 - \frac{2M\varepsilon}{r}}\right). \end{aligned} \quad (\text{A. 15})$$

In (A. 15) the function ${}_1F_1(a, b, c)$ is the confluent hypergeometric function

$${}_1F_1(a, b, c) = \sum_{n=0}^{\infty} \frac{\Gamma(b) \Gamma(a+n) c^n}{\Gamma(b+n) \Gamma(a) n!}. \quad (\text{A. 16})$$

Expressions (A. 12) together with (A. 14) and (A. 15) prove that $F_s(K, R, r)$ satisfy the boundary conditions (6), (7), and the normalization conditions (8).

The functions $v_s(K, r)$ and $\omega_s(K, r)$ are specially chosen so as to satisfy the condition that for $R=r$ the two expressions (A.3) and (A.13) and their derivatives with respect to R should be equal. This yields

$$v_s(K, r) KR f_s(K, R, r)|_{R=r} = \sqrt{KR} \{I_{s+1/2}(KR) + \omega_s(K, r) H_{s+1/2}^{(1)}(KR)\}|_{R=r}$$

and

$$\begin{aligned} v_s(K, r) \frac{\partial}{\partial R} \{KR f_s(K, R, r)\}|_{R=r} &= \frac{\partial}{\partial R} \{\sqrt{KR} I_{s+1/2}(KR)\}|_{R=r} \\ &+ \omega_s(K, r) \frac{\partial}{\partial R} \{\sqrt{KR} H_{s+1/2}^{(1)}(KR)\}|_{R=r}. \end{aligned} \quad (\text{A. 17})$$

These equations, when solved, give for the scattered intensity functions $\omega_s(K, r)$ and the transmitted intensity functions $v_s(K, r)$ the following expressions (cf. formula (11))

$$\omega_s(K, r) = \frac{-W_R \{\sqrt{KR} I_{s+1/2}(KR), KR f_s(K, R, r)\}}{W_R \{\sqrt{KR} H_{s+1/2}^{(1)}(KR), KR f_s(K, R, r)\}} \Big|_{R=r} \quad (\text{A. 18})$$

$$\begin{aligned} v_s(K, r) &= \frac{-W_R \{\sqrt{KR} I_{s+1/2}(KR), \sqrt{KR} H_{s+1/2}^{(1)}(KR)\}}{W_R \{\sqrt{KR} H_{s+1/2}^{(1)}(KR), KR f_s(K, R, r)\}} \Big|_{R=r} \\ &= \frac{\frac{2}{\pi} iK}{W_R \{\sqrt{KR} H_{s+1/2}^{(1)}(KR), KR f_s(K, R, r)\}} \Big|_{R=r} \end{aligned} \quad (\text{A. 19})$$

Introducing the following notations

$$\begin{aligned} a_s &= W_R \{\sqrt{KR} I_{s+1/2}(KR), KR f_s(K, R, r)\}|_{R=r} \\ b_s &= W_R \{\sqrt{KR} Y_{s+1/2}(KR), KR f_s(K, R, r)\}|_{R=r}, \end{aligned} \quad (\text{A. 20})$$

where $Y_{s+1/2}(KR)$ is the Bessel function of the second kind, we have

$$\cos \sigma_s(K, r) = \frac{b_s}{\sqrt{a_s^2 + b_s^2}}; \quad \sin \sigma_s(K, r) = \frac{a_s}{\sqrt{a_s^2 + b_s^2}} \quad (\text{A. 21})$$

$$\omega_s(K, r) = \frac{-a_s}{a_s + b_s i} \quad (\text{A. 22})$$

$$v_s(K, r) = \frac{-\frac{2}{\pi} iK}{a_s + b_s i} \quad (\text{A. 23})$$

$$N_s(K, r) = e^{-i\sigma_s(K, r)} = i \sqrt{\frac{a_s + b_s i}{a_s - b_s i}} \quad (\text{A. 24})$$

$$N_s(K, r) v_s(K, r) = \frac{\frac{2}{\pi} K}{\sqrt{a_s^2 + b_s^2}} \quad (\text{A. 25})$$

$$F_s(K, R, r) = \frac{\frac{2}{\pi} K^2 R f_s(K, R, r)}{\sqrt{a_s^2 + b_s^2}} \quad \text{for } R \leq r. \quad (\text{A. 26})$$

Formula (A. 26) proves that the functions $F_s(K, R, r)$ are real only if the functions $f_s(K, R, r)$ are real. With the help of (A. 15) and of contour representation of confluent hypergeometrical functions (Frank and Mises 1935), we can easily prove that the functions $f_s(K, R, r)$ are real. We use thereby the following symmetrical representation of these functions

$$f_s(K, R, r) = \left(2R \sqrt{K^2 - \frac{2M\varepsilon}{r}} \right)^s \oint e^{iR \sqrt{K^2 - \frac{2M\varepsilon}{r}} (t+i)} \sqrt{K^2 - \frac{2M\varepsilon}{r}}^{s+} (t-i) \sqrt{K^2 - \frac{2M\varepsilon}{r}}^{s-} dt, \quad (\text{A. 27})$$

where the path of integration surrounds the points i and $-i$. We see that the functions $f_s(K, R, r)$ represented by (A. 27) are real, as they do not change when i is replaced by $-i$.

Appendix B

The integrals such as

$$A_u(K, Z, r) = \int_0^Z \{F_l(K, R, r)\}^2 dR \quad (\text{B. 1})$$

occurring in (17) may be evaluated by means of the relation

$$A_u(K, Z, r) = \frac{1}{2K} \{ \partial_K F_l(K, Z, r) \partial_Z F_l(K, Z, r) - F_l(K, Z, r) \partial_K \partial_Z F_l(K, Z, r) \}, \quad (\text{B. 1a})$$

where $\partial_K = \frac{\partial}{\partial K}$; $\partial_Z = \frac{\partial}{\partial Z}$.

This relation is a consequence of the two following equations

$$L_2 F_l(K, R, r) = -K^2 F_l(K, R, r), \quad (\text{B. 2})$$

$$L_2 F_l(t, R, r) = -t^2 F_l(t, R, r); \quad (\text{B. 3})$$

where L_2 denotes, as before, (see equation (13)), the operator

$$\left[\frac{d^2}{dR^2} - 2M\varepsilon V(R, r) - \frac{l(l+1)}{R^2} \right].$$

Subtraction of (B. 3) multiplied on the left by $F_l(K, R, r)$ from (B. 2) multiplied on the left by $F_l(t, R, r)$ gives after intergration

$$W_R\{F_l(t, R, r), F_l(K, R, r)\}\Big|_{R=0}^{R=Z} = (t^2 - K^2) \int_0^Z F_l(t, R, r) F_l(K, R, r) dR, \quad (\text{B. 4})$$

where $W_R\{F_l(t, R, r), F_l(K, R, r)\}$ denotes as usual the Wronskian of the functions $F_l(t, R, r)$ and $F_l(K, R, r)$.

Dividing both sides of equation (B. 4) by $t^2 - K^2$ and evaluating by means of de l'Hospital's rule the expression

$$\lim_{t \rightarrow K} \frac{W_Z\{F_l(t, Z, r), F_l(K, Z, r)\}}{t^2 - K^2},$$

we obtain formula (B. 1).

When the interval of integration in this formula is sufficiently large, we can use for the functions $F_l(K, R, r)$ the asymptotic expressions (A. 12). The derivatives $\partial_Z F_l(K, Z, r)$, $\partial_K F_l(K, Z, r)$, $\partial_K \partial_Z F_l(K, Z, r)$ can be also calculated by differentiation of the asymptotic expressions (A. 12). This is legitimate because these derivatives too possesses asymptotic expansions, namely

$$\partial_Z F_l(K, Z, r) \rightarrow \sqrt{\frac{2}{\pi}} K \cos \{KZ - \frac{1}{2}\pi l + \sigma_l(K, r)\}, \quad (\text{B. 5})$$

$$\partial_K F_l(K, Z, r) \rightarrow \sqrt{\frac{2}{\pi}} [Z + \partial_K \sigma_l(K, r)] \cos \{KZ - \frac{1}{2}\pi l + \sigma_l(K, r)\}, \quad (\text{B. 6})$$

$$\begin{aligned} \partial_K \partial_Z F_l(K, Z, r) &\rightarrow \sqrt{\frac{2}{\pi}} [\cos \{KZ - \frac{1}{2}\pi l + \sigma_l(K, r)\} \\ &\quad - K \{Z + \partial_K \sigma_l(K, r)\} \sin \{KZ - \frac{1}{2}\pi l + \sigma_l(K, r)\}]. \end{aligned} \quad (\text{B. 7})$$

These expressions allow us to calculate the integrals of the type $A_u(K, Z, r)$ and $C_u(K, Z, r)$ for sufficiently large intervals of integration. In fact

$$A_u(K, Z, r) \rightarrow \frac{1}{\pi} \left[Z + \partial_K \sigma_l(K, r) - \frac{1}{2K} \sin 2 \{KZ - \frac{1}{2}\pi l + \sigma_l(K, r)\} \right], \quad (\text{B. 8})$$

$$\begin{aligned} C_u(K, Z, r) &\rightarrow \frac{1}{2\pi} \left[\partial_r \partial_K \sigma_l(K, r) \right. \\ &\quad \left. - \frac{1}{K} \partial_r \sigma_l(K, r) \cos 2 \{KZ - \frac{1}{2}\pi l + \sigma_l(K, r)\} \right]. \end{aligned} \quad (\text{B. 9})$$

To solve the system of equations (17) for $Z \rightarrow \infty$ one needs only to know the potentials (19). From (B. 8) and (B. 9) it follows that

the potentials $V_u(K, r)$ vanishes. In order to calculate the potentials $U_u(K, r)$, we split the integral $B_u(K, Z, r)$ as follows

$$B_u(K, Z, r) = \int_0^r F_l(K, R, r) \partial_r^2 F_l(K, R, r) dR \\ + \int_r^Z F_l(K, R, r) \partial_r^2 F_l(K, R, r) dR. \quad (\text{B. 10})$$

It suffices to calculate the second integral only; for this purpose we differentiate twice expression (A. 11) and obtain

$$\partial_r^2 F_l(K, R, r) = -F_l(K, R, r) [\{\partial_r \sigma_l(K, r)\}^2 + i \partial_r^2 \sigma_l(K, r)] \\ + [\partial_r^2 \omega_l(K, r) - 2i \partial_r \omega_l(K, r) \partial_r \sigma_l(K, r)] \sqrt{KR} H_{l+1/2}^{(1)}(KR) e^{-i\sigma_l(K, r)}. \quad (\text{B. 11})$$

We have therefore

$$\int_r^Z F_l(K, R, r) \partial_r^2 F_l(K, R, r) dR = -\{[\partial_r \sigma_l(K, r)]^2 \\ + i \partial_r^2 \sigma_l(K, r)\} \int_r^Z \{F_l(K, R, r)\}^2 dR + e^{-2i\sigma_l(K, r)} [\partial_r^2 \omega_l(K, r) \\ - 2i \partial_r \omega_l(K, r) \partial_r \sigma_l(K, r)] \left[\int_r^Z KR I_{l+1/2}(KR) H_{l+1/2}^{(1)}(KR) dR \right. \\ \left. + \omega_l(K, r) \int_r^Z \{\sqrt{KR} H_{l+1/2}^{(1)}(KR)\}^2 dR \right]. \quad (\text{B. 12})$$

Making use of the well-known asymptotic expressions for Bessel, Neumann and Hankel functions and of the following relation

$$\int_r^Z KR H_{l+1/2}^{(2)}(KR) I_{l+1/2}(KR) dR = \frac{1}{2K} \left| \partial_K \sqrt{KR} H_{l+1/2}^{(1)}(KR) \partial_R \sqrt{KR} I_{l+1/2}(KR) \right. \\ \left. - \sqrt{KR} I_{l+1/2}(KR) \partial_K \partial_R \sqrt{KR} H_{l+1/2}^{(1)}(KR) \right|_{R=r}^{R=Z}, \quad (\text{B. 13})$$

we can write the integral $B_u(K, Z, r)$ by means of (B. 1), (B. 8), (B. 10), (B. 11) in the form

$$B_u(K, Z, r) = \frac{Z}{\pi} [e^{-2i\sigma_l} \{\partial_r^2 \omega_l - 2i \partial_r \omega_l \partial_r \sigma_l\} - i \partial_r^2 \sigma_l] \\ - \{\partial_r \sigma_l(K, r)\}^2 \frac{Z}{\pi} + P(K, r). \quad (\text{B. 14})$$

By successive differentiation with respect to r of relation (A. 10) it is easy to prove that the first expression in square brackets on the right-hand side of (B.14) vanishes. Thus (cf. (B. 8))

$$\lim_{Z \rightarrow \infty} \frac{B_u(K, Z, r)}{A_u(K, Z, r)} = -U_u(K, r) = -\{\partial_r \sigma_l(K, r)\}^2. \quad (\text{B. 15})$$

Making use of (A. 10), (A. 18) and of the following equations resulting from (12) and (13)

$$\begin{aligned} & \frac{d}{dR} W_R \{ \sqrt{KR} I_{l+1/2}(KR), KR f_l(K, R, r) \} \\ &= 2M\varepsilon V_0(R, r) \sqrt{KR} I_{l+1/2}(KR) KR f_l(K, R, r), \end{aligned} \quad (\text{B. 16})$$

$$\begin{aligned} & \frac{d}{dR} W_R \{ \sqrt{KR} H_{l+1/2}^{(1)}(KR), KR f_l(K, R, r) \} \\ &= 2M\varepsilon V_0(R, r) \sqrt{KR} H_{l+1/2}^{(1)}(KR) KR f_l(K, R, r), \end{aligned} \quad (\text{B. 17})$$

we have in the notation of Appendix A

$$U_u(K, r) = e^{-4i\sigma_l} \left(\frac{2}{\pi} \right)^2 K^2 \quad (\text{B. 18})$$

$$\left[\frac{2M\varepsilon V_0(R, r) \{KR f_l(K, R, r)\}^2 + W_R \{KR f_l(K, R, r), \partial_r KR f_l(K, R, r)\}^2}{(a_l + ib_l)^2} \right]_{R=r},$$

this formula being a consequence of the differentiation of equation (A. 10) with respect to r . Due to (A. 24) and (A. 25) equation (B. 18) can be written

$$\begin{aligned} U_u(K, r) &= \frac{\pi^2}{4K^2} \left[2M\varepsilon V_0(R, r) F_l^2(K, R, r) \right. \\ &\quad \left. + \frac{4}{\pi^2} \frac{W_R \{K^2 R f_l, \partial_r K^2 R f_l\}^2}{(a_l^2 + b_l^2)} \right]. \end{aligned} \quad (\text{B. 19})$$

With the help of the equation

$$\begin{aligned} & W_R \{K^2 R f_l(K, R, r), \partial_r K^2 R f_l(K, R, r)\} \Big|_{R=0}^{R=r} \\ &= 2M\varepsilon K^2 \int_0^r \frac{\partial V_0(R, r)}{\partial r} [KR f_l(K, R, r)]^2 dR \end{aligned} \quad (\text{B. 20})$$

and due to definition (5), equation (B. 19) transforms into

$$U_u(K, r) = \frac{1}{v^2} \left\{ \frac{\pi\varepsilon}{r^2} \int_0^r [F_l(K, R, r)]^2 dR \right\}^2. \quad (\text{B. 21})$$

Making use of an equation analogous to (B. 1) and of the relation

$$\begin{aligned} \frac{df_l(K, R, r)}{dR} &= \left\{ \frac{l}{R} - \frac{M\varepsilon}{(l+1)} \right\} f_l(K, R, r) \\ &\quad - \frac{K_r \left\{ \frac{M^2 \varepsilon^2}{K_r^2} + (l+1)^2 \right\}}{2(l+1)^2 \{2(l+1)+1\}} f_{l+1}(K, R, r), \end{aligned} \quad (\text{B. 22})$$

we obtain the following formula for the potential

$$\begin{aligned} U_l(K, r) &= \frac{1}{v^2} \left(\frac{\varepsilon}{\pi} \frac{K K_r \left\{ \frac{M^2 \varepsilon^2}{K_r^2} + (l+1)^2 \right\}}{(l+1)^2 \{2(l+1)+1\}} [f_l(K, r, r) \partial_K f_{l+1}(K, r, r) \right. \\ &\quad \left. - f_{l+1}(K, r, r) \partial_K f_l(K, r, r)] \right)^2 \frac{K^4}{(a_l^2 + b_l^2)^2}. \end{aligned} \quad (\text{B. 23})$$

where

$$K_r = \sqrt{K^2 - \frac{2M\varepsilon}{r}}. \quad (\text{B. 24})$$

When the velocity of particle (R) is greater than 1 equation (B. 21) can be written with the help of expansion (42) as follows

$$\begin{aligned} U_{00}(K, r) &= \frac{1}{v^2} \frac{1}{r^2} \left[1 - \frac{\sin 2Kr}{2Kr} \right]^2 + \frac{1}{v^2} 0 \left\{ \frac{1}{v^2} \right\}, \\ U_{11}(K, r) &= \frac{1}{v^2} \frac{1}{r^2} \left[1 + \frac{\sin 2Kr}{2Kr} - \frac{2 \sin^2 Kr}{K^2 r^2} \right]^2 + \frac{1}{v^2} 0 \left\{ \frac{1}{v^2} \right\}, \\ U_{22}(K, r) &= \frac{1}{v^2} \frac{1}{r^2} \left[1 - \frac{\sin 2Kr}{2Kr} + \frac{6}{K^2 r^2} \left(\frac{2 \sin 2Kr}{2Kr} - \frac{\sin^2 Kr}{K^2 r^2} - \cos^2 Kr \right) \right]^2 \\ &\quad + \frac{1}{v^2} 0 \left\{ \frac{1}{v^2} \right\}. \end{aligned} \quad (\text{B. 25})$$

It is easy to evaluate the potential $U_{l,s}^l(K, r)$ with the help of du Bois Reymond's second mean value theorem. Thus, we can write the integral $D_{l,s}^l(K, Z, r)$ in the form

$$\begin{aligned} D_{l,s}^l(K, Z, r) &= r \left[\int_{\xi(r)}^r \frac{F_l(K, R, r) F_s(K, R, r)}{R^2} dR \right. \\ &\quad \left. + \int_r^{\xi(Z)} \frac{F_l(K, R, r) F_s(K, R, r)}{R^2} dR \right] \dots \end{aligned} \quad (\text{B. 26})$$

and due to the formula

$$\begin{aligned} & \frac{d}{dR} W_R \{F_s(K, R, r), F_l(K, R, r)\} \\ &= \frac{l(l+1) - s(s+1)}{R^2} F_s(K, R, r) F_l(K, R, r) \end{aligned} \quad (\text{B. 27})$$

we get

$$\begin{aligned} D_{l,s}^j(K, Z, r) &= \frac{r}{(l-s)(l+s+1)} \{W_\xi[F_s\{K, \xi(z), r\}, F_l\{K, \xi(z), r\}] \\ &\quad - W_\xi[F_s\{K, \xi(r), r\}, F_l\{K, \xi(r), r\}]\}. \end{aligned} \quad (\text{B. 28})$$

For sufficiently large values of Z we can use here the asymptotic expressions (A. 12) and (B. 5) for $F_l(K, \xi, r)$, $F_s(K, \xi, r)$, $\partial_\xi F_l(K, \xi, r)$, $\partial_\xi F_s(K, \xi, r)$ and thus obtain

$$\begin{aligned} D_{l,s}^j(K, Z, r) &\sim \frac{r}{(l-s)(l+s+1)} \left(K \sin \left\{ \sigma_s(K, r) - \sigma_l(K, r) \right. \right. \\ &\quad \left. \left. + \frac{\pi}{2} (l-s) \right\} - W_\xi[F_s\{K, \xi(r), r\}, F_l\{K, \xi(r), r\}] \right). \end{aligned} \quad (\text{B. 29})$$

It results from (B. 29) that the potential $U_{l,s}^j(K, r)$ vanish.

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A NEW SIMPLE TYPE OF THE RECTANGULAR PULSE GENERATOR

by Olgierd K. DASZKIEWICZ, 2nd Physical Laboratory, Jagellonian University, Cracow

(received July 1, 1950)

Description of a simple rectangular pulse generator with regulation of pulse duration, consisting of a cathode coupled multivibrator and a paraphase degenerative amplifier.

Rectangular pulse generators have nowadays a very wide field of applications in nuclear physics, radar engineering, wireless engineering, and in different other science industries. The generators so far being used require for their construction a rather complicated equipment, especially when possessing: (a) a regulation of distances between the pulses with maintenance of constant frequency as far as possible, or (b) a device for ascertaining the independence of the pulse amplitudes on the fluctuations of the frequency, which may be precisely regulated between wide limits.

The best method of generating rectangular pulses is that of the multivibrator circuit. This method has the following advantages: (1) only pure electronic processes take place in the circuit, (2) the driving and the synchronization of the multivibrator circuit is very easy, (3) the pulses have a quite definite shape and time of duration.

In the present communication a simple construction of a generator possessing all the above mentioned advantages is reported. The circuit diagram is shown in fig. 1. The two first valves are working as a cathode coupled multivibrator. Due to some alterations of the classical cathode coupled multivibrator circuit the reported generator produces rectangular pulses for a very wide range of different elements, especially of those influencing the frequency. An important role is also played by the limiting resistances which have been introduced for the conservation of rectangular shape and constant amplitude of the pulses

at every value of RC , establishing thus the frequency and the length of the pulses. At the same time these resistances diminish the given range of frequencies and the length of the pulses. The third valve is working as a cathode follower or as a paraphase degenerative amplifier. In the first case it is used as a buffer-stage; in the second one, besides the separation, one can simultaneously receive pulses differing in phase by π . Another application of this valve is foreseen: This valve

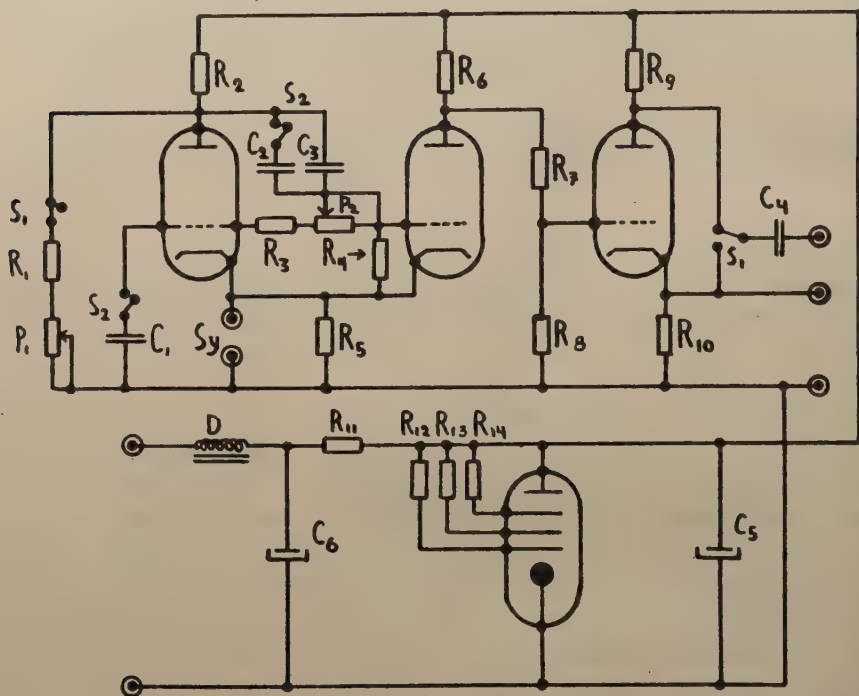


Fig. 1. The circuit of the generator. $R_1 = 50 \text{ K}\Omega$, $R_2 = 20 \text{ K}\Omega$, $R_3 = 50 \text{ K}\Omega$, $R_4 = 1 \text{ M}\Omega$, $R_5 = 100 \text{ K}\Omega$, $R_6 = 20 \text{ K}\Omega$, $R_7 = 1,5 \text{ M}\Omega$, $R_8 = 150 \text{ K}\Omega$, $R_9 = R_{10} \text{ K}\Omega$, $R_{11} = 3 \text{ K}\Omega$, $R_{12} = R_{13} = R_{14} = 500 \text{ K}\Omega$; $P_1 = P_2 = 1 \text{ M}\Omega \log.$; $C_1 = 300 \text{ pF}$, $C_2 = 5000 \text{ pF}$, $C_3 = 300 \text{ pF}$, $C_4 = 0,1 \text{ }\mu\text{F}$, $C_5 = C_6 = 16 \text{ }\mu\text{F}$. All triodes are AC 2.

can be also used in a special circuit transforming rectangular pulses into very short and steep triangular pulses. The transition from the first action to the second one is obtained in a very simple manner by shunting of the plate resistance by a small inductivity. In the case of such a use of the valve it is necessary to insert an additional stage containing a valve working in the C -class, i. e. with a large negative grid bias, the grid being connected to the proper generator by a differential circuit of a suitable small time constant. The frequency and

the shape of the vibrations are defined by all elements of the multivibrator. The elements under control are:

(1) The potentiometer P_2 .

(2) The capacities C_1 , C_2 and C_3 , which can be switched on when changing the bands. The resistance R_3 , although it is shortening the band, is used in order to avoid the same potential on the two grids at an extreme position of the potentiometer P_2 , since in this case vibrations could be deformed or even annihilated. For the high frequency band the first valve grid is not earthed through a condenser, the mounting capacity of the circuit being sufficient and, of course, necessary in this case.

The control of the length of the pulses is obtained by changing the average plate voltage of the multivibrator valves. Increasing this voltage on one plate is equivalent to diminishing it on the other plate. The change of this voltage could be obtained by increasing or diminishing the plate resistance, or by potentiometrical supplying of the plate. The latter device, as more convenient and stable in operation, has been used in the apparatus. For ensuring continuous regulation and avoiding deformations or decay of the vibrations, the potentiometer P_1 is connected in series with a limiting resistance R_1 .

It has been observed that if the ratio of the time interval between two consecutive pulses to the length of the pulses remains within the limits of $1/3$ to 3, the frequencies of the pulses are quite negligibly influenced by changing the length of the pulses.

It has been already stated that even for a very wide frequency band rectangular pulses can be obtained by using, particularly for higher frequencies, additional elements for correcting the shape of the pulses, e. g., for frequencies exceeding 20,000 pulses/sec the cathode resistance of the multivibrator must be blocked by a suitable capacitor, especially when the plate resistances are different.

As the synchronizing voltage should be applied also to the cathode resistance, an output valve is used of the same type as the multivibrator valve, since in this case no large output power is required. This valve works as a cathode follower and or a paraphase degenerative amplifier. A potentiometric supply of the control grid of this valve is very important as by a suitable choice of the resistances of the divider the most profitable working point can be found. A capacitance coupling was not used on account of its dependence on frequency. This direct coupling is the most convenient, because it is smoothing out and properly shaping the pulses.

The generator contains two frequency bands: 14 c/sec—5 kc/sec and 4 kc/sec—20 kc/sec. The output pulses have an amplitude of 1 V.

Fig. 2 represents the shape of some pulses obtained on the screen of a „Furzehill“ cathode ray oscilloscope. Good filtration and stabilization of the supply voltages are of importance. In the circuit a stabilizing valve STV 280/40 was used.

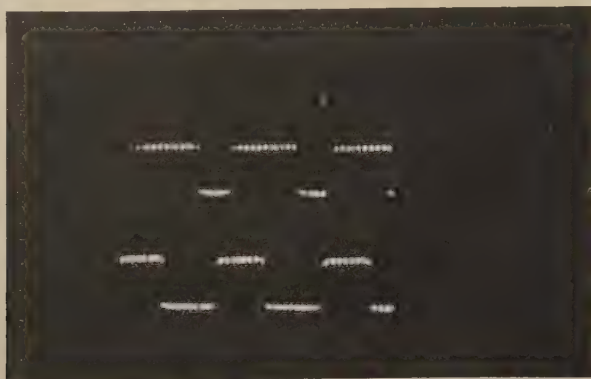


Fig. 2. The shape of the pulses.

I wish to express my gratitude to Professor H. Niewodniczański for enabling me the construction of this generator in his Laboratory and for many valuable discussions which materially accelerated the carrying out of this work.

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ON THE ANGULAR DISTRIBUTION OF ELECTRON PAIRS CREATED IN LEAD BY GAMMA-RAYS OF ThC''

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(received July 1, 1950)

The angular distribution of electron pairs created in lead by γ -rays of ThC'' has been measured by the method of the Geiger-Müller counters. The results do not agree with the theory of Bethe and Heitler, and seems to indicate that the Born approximation used in that theory is not adequate to the problem in question.

Introduction

The absorption of hard γ -rays consists of the following three processes: (a) Photoelectric effect, (b) Compton effect, and (c) Production of electron pairs. The absorption produced by the photoelectric process and the Compton effect can be calculated from Sauter's and Klein-Nishina's formulae. Experimental values for the cross sections and the angular distributions are very close to those calculated from these formulae.

Since 1930 several investigations have shown that the absorption coefficient for hard γ -rays in heavy elements is much greater than it should be if only the photoelectric and Compton processes were effective. In 1932 Chao reported finding a secondary γ -radiation of the energy about 0,5 MeV, accompanying the process of the absorption of hard γ -rays. Gray & Tarrant and Meitner & Hupfeld showed that this secondary radiation did not depend on the energy of primary γ -rays, on the kind of absorbing material and on the angle between the direction of observation and that of the primary photons.

After the appearance of Dirac's relativistic theory of the electron and Anderson's discovery on the positon Blackett and Occhialini suggested that for the increase of the absorption coefficient of hard γ -rays the production of electron pairs was responsible.

Theories of the production of electron pairs in the field of a nucleus

Bethe and Heitler (1934) published a theory of pair creation in the field of a nucleus, in which they applied the Born approximation. In this approximation the electrostatic interaction between the nucleus, the positron, and the negaton is neglected. Owing to that Bethe and Heitler obtained the same energies and the same angular distributions for both electrons; these distributions were also independent of the atomic number Z of the absorber. In the formula given by Bethe and Heitler the differential cross-section for the production of electron pairs depends on the angles given in fig. 1. The distribution of each

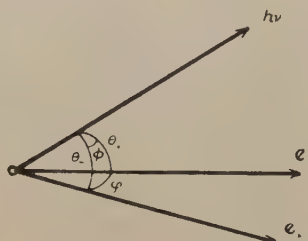


Fig. 1. Designations of the angles.

angle can be obtained by integration of Bethe and Heitler's formula over all other parameters.

Jaeger and Hulme (1935, 1936) and Jaeger (1936) took into account the action of the electrostatic field of the nucleus on the negaton and the positron. The calculations with exact relativistic wave functions were extremely tedious but Jaeger and Hulme succeeded in showing that Bethe and Heitler's formula is not valid for photons of energy 2,6 MeV. For this energy and an atomic number Z of about 80 they showed by numerical integration that the mean angle between the directions of both electrons was about two times greater than that calculated on the ground of the theory of Bethe and Heitler. Moreover Jaeger and Hulme have shown that the mean angle between the directions of the photon and the negaton ($\bar{\theta}_-$) and the mean angle between the directions of the photon and the positron ($\bar{\theta}_+$) depend on the atomic number of the absorber, increasing slowly with Z .

Previous experimental results on the angular distribution of electron pairs

The angular distribution of electron pairs created by the γ -rays of ThC'' was investigated by several authors. The measurements concerned mainly the values of the angle $\bar{\phi}$, i. e., the mean angle between

the directions of both electrons. All these investigations can be divided into two groups: (a) those making use of the cloud-chamber method and (b) the other, making use of the Geiger-Müller counter method.

a) Klarmann and Bothe (1936), who employed the cloud chamber method, obtained for krypton ($Z=36$) $\bar{\varphi}=16^\circ$ and for xenon ($Z=54$) $\bar{\varphi}=42^\circ$, and concluded that the angle $\bar{\varphi}$ depends markedly on Z . This conclusion seems not to be very well based, as for krypton $\bar{\varphi}$ was obtained from four values only: 8° , 9° , 10° and 48° .

Simons and Zuber (1937) obtained for argon ($Z=18$) $\bar{\varphi}=30^\circ$ and for methyl iodide (for iodine $Z=53$) $\bar{\varphi}=32^\circ$. These values were very close to those following from Bethe and Heitler's theory.

In a series of works Groshev and Frank (e. g., 1938, 1945) found for nitrogen ($Z=7$) $\bar{\varphi}=40^\circ$, for krypton ($Z=36$) $\bar{\varphi}=48^\circ$ and for xenon ($Z=54$) $\bar{\varphi}=52^\circ$. These results were in favour of the theory of Jaeger and Hulme, showing a dependence of $\bar{\varphi}$ on Z .

b) Adam (1937) using the Geiger-Müller counter method obtained for lead ($Z=82$) $\bar{\varphi}=30^\circ$ in good accord with Bethe and Heitler's theory. The result of Niewodniczański and Pisklak (1939) for electron pairs produced in lead by γ -rays of radium were in agreement with this theory too, while the measurements of Alichanian, Dzelepov and Spivak (1938) yielded much greater values for $\bar{\varphi}$.

Formulation of the problem and theoretical calculations

The purpose of the present investigation was to determine experimentally the distribution of the angle between the directions of the photon and one of the electrons (θ_2) keeping the value of the angle between the directions of the photon and the second electron (θ_1) fixed, and to compare the results with the conclusions drawn from the theory of Bethe and Heitler.

For small photon energies (about mc^2) the analytic integration of Bethe and Heitler's formula is not possible, but it can be performed numerically. The angular distribution of electron pairs created by 2,62 MeV photons (emitted by ThC'') were calculated by Groshev (1945) on the basis of the theory of Bethe and Heitler. Similar calculations of the distribution of the angle θ_2 , the angle θ_1 being fixed, were performed (for $\Phi=180^\circ$) in connection with the present investigation. It was assumed thereby that both electrons of each pair possess equal energies. This assumption represents the most probable case according to both existing theories of the effect. Moreover, it may be considered as particularly legitimate in the present investigation as two electrons of equal energy are more likely to penetrate through the lead foil and the counter windows than any other combination of two electrons

with the same total energy. The calculations were performed for a smaller range of angles than that of Groshev, but more curves were drawn (for a greater number of fixed values of θ_1) and more points were taken for each curve.

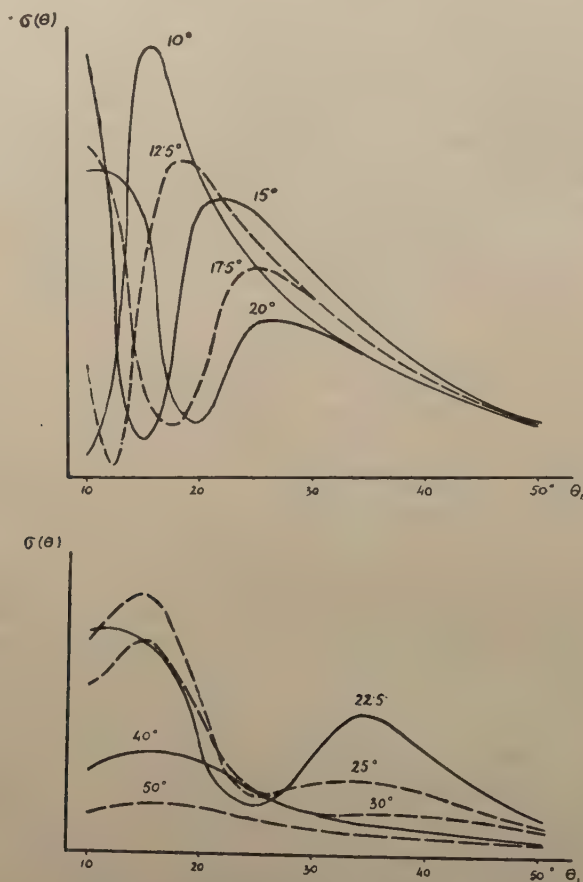


Fig. 2. Theoretical distribution of θ_2 .

The obtained theoretical curves are represented in fig. 2. It follows from this figure that the curves have two maxima transforming one into another and the minima for $\theta_2 = \theta_1$.

The source of the γ -rays

The source of γ -rays was a MsTh sample contained in several platinum needles equivalent to 39 mg of radium, prepared in 1945 by the Auer Gesellschaft in Vienna. In the spectrum of the γ -radiation of this MsTh-sample the main part is played by $\text{Th}(C + C'')$, the

2,62 MeV line being by far the most intensive. In this case the effective spectrum for pair production can be obtained from that reported by Alichanow and Latyshev (1940) by taking into account: (a) the absorption of the γ -rays in a 2,5 cm lead filter, which was used in order to diminish the intensity of the lower energy γ -lines and (b) the dependence of the pair production cross-section upon the photon energy.

The effective spectrum calculated in such a manner is given in fig. 3., where the intensities of all lines are represented in comparison to the intensity of the 2,62 MeV line.

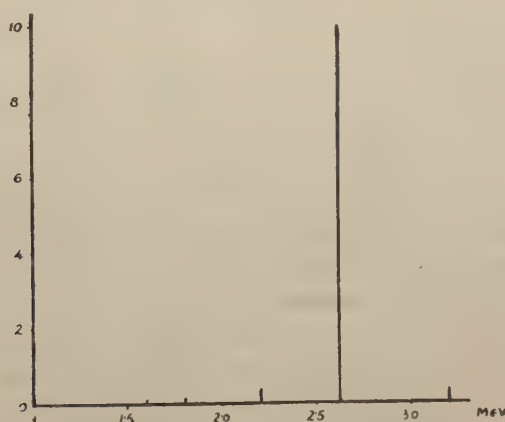
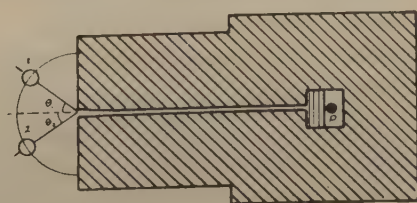


Fig. 3. The effective γ -rays spectrum of $\text{Th}(C+C'')$.

The MeTh-sample was put inside a lead block composed of lead bricks and provided with a collimation channel through which a narrow beam of γ -rays was transmitted (fig. 4). This channel was 30 cm long,



Scale 1:10

Fig. 4. Geometry of the apparatus. P : MsTh sample, 1,2: G. M. counters.

2,5 cm high and its width was changing from 0,5 cm at the beginning to 1 cm at the end in order to diminish the background of secondary electrons originating in the walls of the channel.

The construction of the Geiger-Müller counters

The Geiger-Müller counters for β -radiation were made of brass tubes of 16 mm external diameter and 1 mm wall thickness. The construction details are represented in fig. 5. This is a modified construction worked out in the Physical Laboratory of the Mining Academy in Cracow.

The counters possess mica-windows, $2,5 \times 1,0$ cm, 20μ thick. Windows of this thickness transmit all electrons of energy exceeding 60 keV. The effective counter-length was limited to 3,5 cm by glass tubes surrounding the anode wire. The whole counter was 15 cm long. Owing to this it contained a rather great amount of gases assuring a correspondingly longer life time.

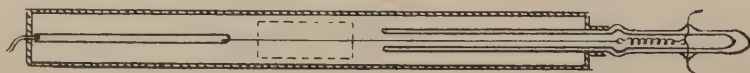


Fig. 5. The Geiger-Müller counter for β radiation.

The counters were filled with the usual mixture of argon (90 mm Hg) and alcohol vapour (10 mm Hg). The counter threshold lay at about 920 V and the mean length of the plateau was 200 V. The slope of the plateau on its whole length did not exceed 5%. Eight such counters were prepared to allow continuous work despite any troubles with the counters.

The electronic equipment

The electronic part of the apparatus consisted of three main circuits: (a) the high voltage generator and stabilizer, (b) the coincidence circuit, and (c) the counting rate meter.

The high voltage generator supplying the counters had a neon tube stabilization with a potentiometer output. The voltage could be continuously changed from 500 to 1400 V.

The coincidence circuit is represented in fig. 6. The first stage of this circuit consisted of a double triode (6N7) working as a fast multivibrator. The counter anode was connected directly (without coupling capacitor) to the valve grid; owing to this the impulse amplitude is increased and its duration appreciably decreased. The negative impulse from the anode of the multivibrator circuit was supplied through a very low capacity (6 pF) to the grid of the Rossi circuit valve (AF 100). The resolving time of the circuit could be changed by applying a positive bias (up to 2 V) to the grid of the pentode. The limits of these changes, measured by the method of accidental coincidences, were

$$3 \times 10^{-7} - 1,7 \times 10^{-6} \text{ sec.}$$

The counting rate meter consisted of a slow multivibrator circuit increasing the impulse amplitude and its duration, and a power pentode with telephone call meter included in its plate circuit.

The following auxiliary circuits were also used:

(a) an anode voltage generator supplying the coincidence circuit and the counting rate meter,

(b) a scaler of 64 (after E. Baldinger) for control counting of impulses from each counter separately.

All circuits were supplied by 220 V A.C. mains through a magnetic voltage stabilizer. In the primary circuit an electromagnetic relays was included to prevent counting after each momentary interruption of the A. C. supply.

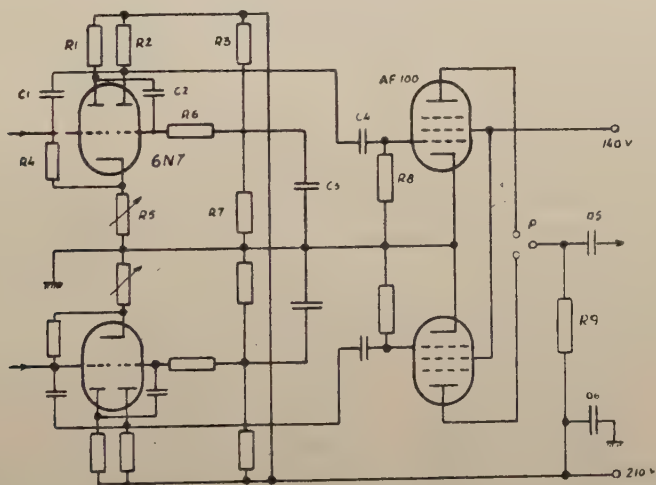


Fig. 6. The coincidence circuit. $C_1 = C_2 = 15 \text{ pF}$, $C_3 = C_5 = 1 \mu\text{F}$, $C_4 = 6 \text{ pF}$, $R_1 = 5 \text{ k}\Omega$, $R_2 = 30 \text{ k}\Omega$, $R_3 = 0.5 \text{ M}\Omega$, $R_4 = 10 \text{ k}\Omega$, $R_5 = 3.5 \text{ k}\Omega$, $R_6 = 100 \text{ k}\Omega$, $R_7 = 10 \text{ k}\Omega$, $R_8 = 4 \text{ k}\Omega$, $R_9 = 20 \text{ k}\Omega$.

Measurements and results

The measurements of the angular distribution were carried out by the method of Geiger-Müller counters working in coincidence. The electron pairs were created by γ -rays of MgTh in a 100μ thick lead foil placed at the end of a collimation channel. The counters were fastened in vertical position in grips which could rotate around an axis passing through the end of the collimation channel. The distance of the counters from the lead foil was 8.5 cm. The grips had pointers indicating the position of the counters on an angular scale.

By such a measurement beside the proper coincidences $\beta^-\beta^+$ the following other types of coincidences might also be counted:

(a) accidental coincidences,

(b) $\gamma\gamma$ coincidences, when the photon scattered in the Compton effect in one counter were counted in the second counter,

(c) $\beta^-\gamma$ coincidences, produced by the Compton electron and the scattered photon from the lead foil,

(d) $\beta^+\gamma$ coincidences, produced by the positon and the photon arising by its annihilation,

A discussion of these types of background coincidences showed that:

(a) the accidental coincidences could be omitted because of the short resolving time of the coincidence circuit,

(b) $\gamma\gamma$ coincidences could be omitted because of the very low counter efficiency for γ -radiation,

(c) $\beta^-\gamma$ coincidences could play their part only in the case of the angle between the counters greater than 90° ,

(d) the main source of background coincidences were undoubtedly those of the $\beta^+\gamma$ type.

The $\beta\gamma$ coincidences could be measured by shielding one counter window with a lead sheet thick enough to be impenetrable to electrons. Then, only the coincidences produced by an electron reaching the unshielded counter and a corresponding photon reaching the shielded one could be registered. In order to obtain the true coincidence curve for electron pairs one had to subtract from the curve of all registered coincidences the curves of the $\beta\gamma$ effect for both counters.

In the present investigation the number of coincidences per hour (N_0) was measured versus the angular position of one counter (θ_2), keeping the position of the second counter (θ_1) fixed. Two sets of such measurements for fixed angles $\theta_1=15^\circ$ and $\theta_1=20^\circ$ were made. The results are represented in tables I and II. The second and third columns of these tables contain the numbers of the $\beta\gamma$ coincidences obtained by lead shielding of the first and second counters (N_1, N_2). The last columns contain the differences $N=N_0-(N_1+N_2)$, representing the numbers of the observed electron pairs.

Table I. $\theta_1=15^\circ$.

θ_2	N_0	N_1	N_2	N
10°	45,7	16,4	16,4	$12,9 \pm 1,6$
12,5	42,1	12,7	13,6	$15,8 \pm 1,6$
15	39,7	9,4	11,0	$19,3 \pm 1,4$
17,5	35,0	8,1	9,5	$17,4 \pm 1,3$
20	30,8	7,2	7,2	$16,4 \pm 1,2$
25	28,5	6,8	6,7	$15,0 \pm 1,2$
30	24,7	5,0	5,3	$14,4 \pm 1,0$
40	21,5	4,1	3,1	$14,3 \pm 0,9$

Table II. $\theta_1 = 20^\circ$.

θ_2	N_0	N_1	N_2	N
10°	35,5	9,6	10,3	$15,6 \pm 1,4$
12,5	30,7	8,8	8,9	$13,0 \pm 1,3$
15	27,5	6,9	8,5	$12,1 \pm 1,3$
17,5	26,3	6,2	6,5	$13,6 \pm 1,2$
20	26,0	5,4	5,6	$15,0 \pm 1,3$
25	21,2	4,7	4,2	$12,3 \pm 1,1$
30	20,1	3,8	3,5	$12,8 \pm 1,0$
40	14,9	2,2	2,1	$10,6 \pm 0,9$

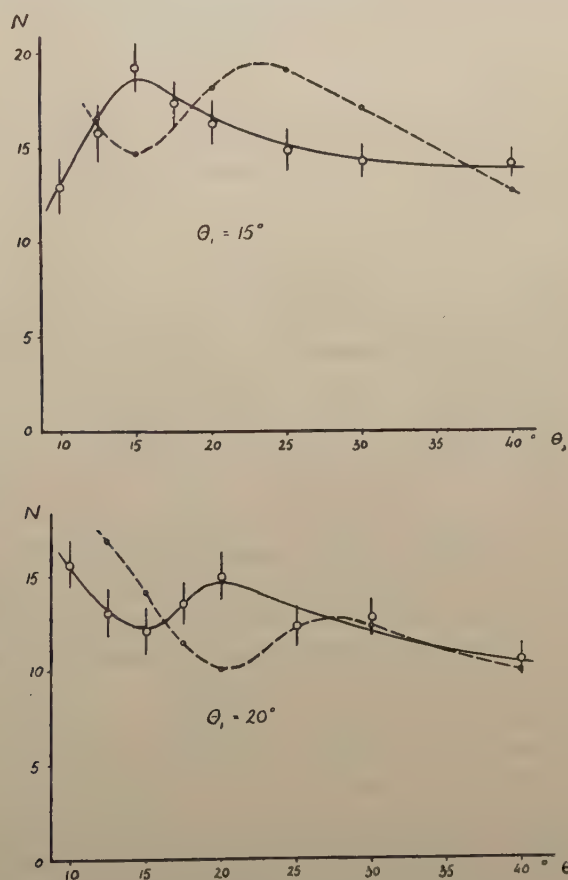


Fig. 7. Comparison of experimental and theoretical curves.

In fig. 7 the numbers N are plotted versus the angle θ_2 for both sets of measurements. The dotted curves represent the theoretical dependence obtained from the corresponding curves in fig. 2 and for the geometry actually existing in the corresponding experiments.

Conclusions

As it is clearly seen from the curves (fig. 7) the experimental maxima are obtained for symmetrical positions of the counters, whereas theoretically minima should then be expected. This result shows that the Born approximation used in the calculations of Bethe and Heitler is not sufficient for obtaining the correct angular distribution of electron pairs.

The author is grateful to Komisja Popierania Twórczości Naukowej i Artystycznej przy Prezydium Rady Ministrów for granting a scholarship and to Professor H. Niewodniczański for submitting the subject of this work and for valuable discussions and encouragement during its course. He also wishes to express his thanks to Mr J. Gierula from the Mining Academy, Cracow, for the filling of the counters and to Dr W. Sucharski from the City Hospital in Bydgoszcz for lending the MsTh sample.

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ON THE SELECTIVE ABSORPTION OF THERMAL NEUTRONS IN SELENIUM AND ARSENIUM

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(received July 1, 1950)

Measurements were made of thermal neutron cross-sections in Se and As. Photoneutrons from a Ra + Be source of strength 100 mg Ra were used. The variation of these cross-sections with energy of the incident neutrons investigated and interpreted as an interference effect in the microcrystals of Se and As.

Introduction

The absorption of neutrons is one of the most interesting problems in nuclear physics. Especially interesting is the problem of the energy dependence of neutron absorption. The knowledge of this dependence provides informations about the nuclear energy levels in nuclei.

The dependence of absorption cross-sections upon the energy of neutrons is well described by Breit-Wigner formula (1936—1946). This formula gives for the thermal energy region a $1/v$ dependence, i. e., proportionality of thermal neutron cross-sections to $E^{-1/2}$.

In a great many cases deviations from the $1/v$ law in the thermal energy region are observed. There are two causes of these deviations: (1) The existence of an energy level in the neighbourhood of the thermal energy region (Cd, Ir, Eu); the capture cross-sections are then very large and their energy dependence is much more complicated. (2) Interference effects occurring in the case when the de Broglie wave lengths of the thermal neutrons are of the order of magnitude of the distances between the lattice planes of the microcrystals of the examined crystalline body. These interference effects are superposed on the proper nuclear effects (Halpern 1941; Fermi 1946, 1947).

The total thermal neutron cross-section (in the absence of energy levels in the neighbourhood of the thermal energy region) may be expressed by:

$$\sigma = a + bE^{-1/2};$$

where a is the scattering cross-section which is practically energy independent, and $bE^{-1/2}$ the capture cross-section, proportional to $1/v$. When interference effects take place, a does not remain constant, showing fluctuations with the change of energy, i. e. with the change of wave length of the impinging neutrons.

Apparatus

A source of photoneutrons from the $\text{Be}(\gamma, n)^2\text{He}$ reaction was used. One hundred of 1 mg radium needles were enclosed in a little cylindrical box filled with beryllium powder. The thickness of the layer of the Be-powder surrounding the Ra-needles was 3 cm, which is equivalent to about 0,5 kg Be (very fine Be-powder). Neutrons were slowed down to thermal energies in a layer of paraffin wax of 6 cm thickness.

In order to provide sufficient safety safeguard against this strong source of γ -radiation the whole neutron source, including the paraffin-wax, was surrounded by 5 cm of lead except the side opposite to the ionization chamber.

The ionization chamber was a brass cylinder of 5 cm length and 5 cm diameter. The collecting electrode was a steel wire of 1 mm diameter possessing at one of its ends a brass plate (38 mm of diameter). The distance between this plate and the bottom of the ionization chamber was 5 mm, it being the optimum depth of the chamber found by experiment. The other end of the collecting electrode was surrounded by a protective ring which served also to fasten the ionization chamber to the wall of a little box containing the preliminary stage of the amplifier. The collecting electrode was insulated from the external electrode by „plexiglass“ (a kind of very well insulating plastics).

The whole ionization chamber with a little box containing the preliminary stage of the amplifier was put inside a larger cadmium box, the internal walls of which were covered by a 2 cm thick layer of cardboard in order to reduce microphonic effects. In front of the ionization chamber aluminium boxes containing powdered absorbing substances were situated, placed in a Cd tube. The Cd box containing the ionization chamber, the absorbers, and the preliminary stage of the amplifier was situated opposite to the neutron source on a wooden base, on elastic rubber sponges in order to diminish the sensibility of the ionization chamber to mechanical disturbances.

The ionization chamber was closed by an aluminium boron-lined lid. (Due to the impossibility of obtaining BF_3 a boron-lined chamber for counting slow neutrons was used). A 3 mg/cm² thick layer of amor-

phous boron powder was experimentally checked to be the most favourable one.

The external electrode of the ionization chamber was on the potential of +400 V, being blocked by an electrolytic condenser (16 μ F) situated inside the Cd box containing the chamber. (This has been found to be very important).

Fig. 1 represents the ionization chamber, the shields, and the preliminary stage of the amplifier.

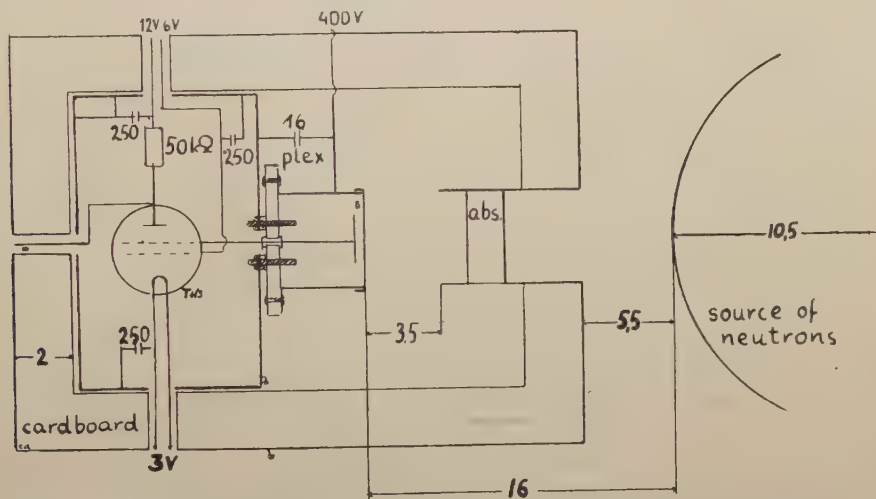


Fig. 1. The ionization chamber and the preliminary stage of the amplifier.

The linear amplifier consisted of the preliminary stage mounted together with the ionization chamber, and of the proper linear amplifier mounted in another shielding box. The preliminary stage was built according to Riezler (1941). The amplifying valve was a two-grid electrometric valve Telefunken T 113. The plate voltage was +12 V, the first grid voltage +6 V, the filament voltage 3 V. All these voltages were obtained from a storage battery. The plate resistance was 50000 Ω . Pulses from the ionization chamber were conducted directly to the second grid of the T 113 — valve.

In order to reduce electromagnetic disturbances from external causes, a very accurate shielding of all electric connections was necessary, especially of those conducting pulses from the preliminary stage to the amplifier and connecting the amplifier with the voltage supplying generator. Finally, the elimination of the electromagnetic disturbances was obtained by blocking all voltage supplies of the electrometric valve by means of electrolytic condensers of $250 \mu\text{F}$ capacity. The proper linear amplifier was built according to Petruskas and Van

Atta (1940). It was a three stage amplifier, linear for input voltages up to 0,6 mV, and possessing for input voltages not exceeding this value an amplification factor of 250 000. Together with the preliminary stage, an amplification factor of 1 000 000 was obtained.

The amplified pulses from the linear amplifier were conducted by a screened wire to the counting device consisting of a 6L6 valve and a telephone call meter. All supply voltages to the amplifier were created in a supply generator. These voltages were stabilized by neon tubes LK 131.

A general outline of the apparatus is represented on fig. 2.

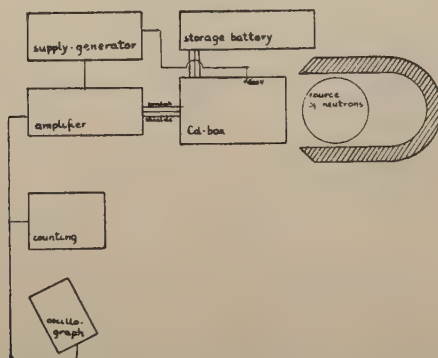


Fig. 2. The locating of the apparatus in the laboratory.

Results

The subject of this work was to measure the absorption cross-sections of selenium and arsenium nuclei for thermal neutrons and to find out how these cross-sections depend on the energy of the neutrons.

On account of the weakness of the neutron source I had to content myself with a not very perfect method of selectioning the velocity of the neutrons, namely the boron absorption method. For this purpose absorption measurements were made with different layers of boron between the source of the neutrons and the absorber. The thickness of these layers of boron was 0 mg B/cm², 21,4 mg B/cm² and 34 mg B/cm².

The absorption cross-section of boron for neutrons is exatly proportional to $E^{-1/2}$, viz.

$$\sigma(E) = 118 \times 10^{-24} \cdot E^{-1/2}. \quad (10)$$

After passing of the neutron beam through a boron layer, more slower than faster neutrons will be absorbed. This behaviour is repre-

sented on fig. 3. The curve *A* represents the Maxwellian distribution with a maximum at 0,026 eV. This curve corresponds to the velocity distribution of the neutron beam before filtering in a boron layer. The following curves (*B* and *C*) represent the velocity distributions of the neutron beams after passing 21,4 mg/cm² and 34 mg/cm² of boron, respectively. It is easy to see that the maximum of these di-

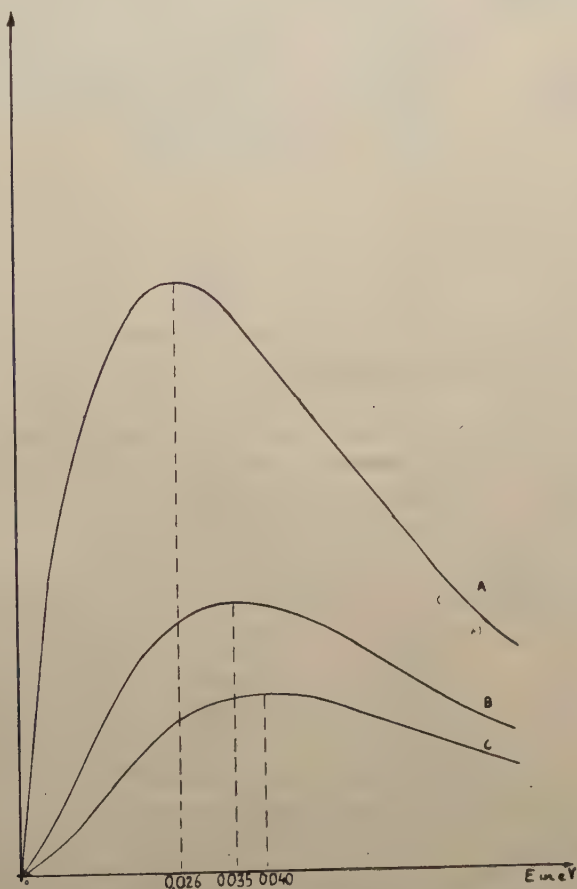


Fig. 3. Velocity distribution curves for unfiltered (*A*) and boron filtered neutron beams (*B* and *C*).

stribution curves is shifted towards higher energies with increasing thickness of boron. From these experiments it is possible to obtain a rough idea of the dependence of the cross-sections for absorption of slow neutrons on their energy. The absorbers (Se and As) were used in a powdered metallic form. They were chemically pure elements, furnished by the „Mikrochemia“ works in Warsaw.

The results of the measurements are represented in the following, tables, where n denotes the registered number of counts per 8 hours, n_0 the background per 8 hours, $I = n - n_0$ the intensity of the neutron beam in counts per 8 hours.

Table I. *Selenium, 0 mg B/cm², $n_0 = 677 \pm 7$.*

Mass in g/cm ²	n	I	$\log I$
0	2296 ± 18	1619 ± 25	$3,209 \pm 0,005$
1,26	2107 ± 20	1430 ± 27	$3,155 \pm 0,006$
3,14	1869 ± 20	1192 ± 27	$3,076 \pm 0,007$
5,78	1525 ± 16	848 ± 23	$2,928 \pm 0,008$

Table II. *Selenium, 21,4 mg B/cm², $n_0 = 677 \pm 7$.*

Mass in g/cm ²	n	I	$\log I$
0	1591 ± 17	914 ± 24	$2,961 \pm 0,008$
1,26	1457 ± 9	780 ± 16	$2,892 \pm 0,005$
3,14	1265 ± 15	588 ± 22	$2,769 \pm 0,009$
5,78	1020 ± 13	343 ± 20	$2,535 \pm 0,016$

Table III. *Selenium, 34 mg B/cm², $n_0 = 529 \pm 14$.*

Mass in g/cm ²	n	I	$\log I$
0	1224 ± 23	695 ± 37	$2,842 \pm 0,015$
3,14	902 ± 17	373 ± 31	$2,572 \pm 0,020$
5,67	779 ± 19	250 ± 33	$2,398 \pm 0,034$

Table IV. *Arsenium, 0 mg B/cm², $n_0 = 529 \pm 14$.*

Mass in g/cm ²	n	I	$\log I$
0	2100 ± 22	1571 ± 36	$3,196 \pm 0,005$
1,26	2024 ± 17	1495 ± 31	$3,175 \pm 0,005$
3,14	1782 ± 17	1253 ± 31	$3,098 \pm 0,006$
4,71	1574 ± 22	1045 ± 36	$3,018 \pm 0,009$
6,28	1465 ± 20	936 ± 34	$2,971 \pm 0,010$

Table V. *Arsenium, 21,4 mg B/cm², $n_0 = 529 \pm 14$.*

Mass in g/cm ²	n	I	$\log I$
0	1403 ± 25	874 ± 39	$2,942 \pm 0,012$
1,26	1361 ± 20	832 ± 34	$2,920 \pm 0,010$
3,14	1250 ± 24	721 ± 38	$2,858 \pm 0,015$
4,71	1212 ± 18	683 ± 32	$2,834 \pm 0,011$
6,28	1100 ± 18	571 ± 32	$2,757 \pm 0,012$

Table VI. *Arsenium, 34 mg B/cm², $n_0 = 529 \pm 14$.*

Mass in g/cm ²	n	I	$\log I$
0	1224 ± 23	695 ± 37	$2,842 \pm 0,015$
3,14	1061 ± 23	532 ± 37	$2,726 \pm 0,018$
6,28	913 ± 13	384 ± 27	$2,584 \pm 0,015$

Fig. 4 and 5 represent the logarithm of the intensity of the neutron beam versus the thickness of the absorber. The dotted lines show the limits of variation of the straight line looked for due to statistical errors of measurement.

On the ground of these experimental data the following figures for the mean cross sections of Se and As nuclei (taking no regard to their isotopic constitution) for the absorption of neutrons of three different energy distributions have been evaluated.

Table VII. *Selenium.*

Thickness of <i>B</i> -layer mg/cm ²	σ (in 10^{-24} cm ²)
0	$15,8 \pm 0,8$
21,4	$22,8 \pm 1,2$
34	$24,4 \pm 2,7$

Table VIII. *Arsenium.*

Thickness of <i>B</i> -layer mg/cm ²	σ (in 10^{-24} cm ²)
0	$10,8 \pm 1,4$
21,4	$8,2 \pm 0,6$
34	$12,1 \pm 1,6$

Discussion

The values obtained for the cross-sections correspond roughly to the most probable energies of the neutrons, though in reality they are averages over the whole energy distribution. The cross-sections obtained for boron filtered neutrons must be attributed to larger neutron energies than for neutrons of Maxwellian velocity distribution. The result obtained for Se for thermal neutrons of Maxwellian velocity distribution is similar to that obtained by Dunning et al. (1935) (12×10^{-24} cm²).

The results obtained indicate that the cross-sections of Se and As nuclei for thermal neutrons are not proportional to $1/v$, but depend on the energy of the neutrons in a more complicated manner. It is improbable that this change may be attributed to the existence of some energy levels in the thermal energy region, because in this case the cross sections should have been much larger.

Therefore the obtained energy dependence must be rather interpreted as the result of elastic scattering in microcrystalline structure of Se and As. This interpretation is supported by the known fact, that elements in the neighborhood of Se and As in the periodic table (e. g. Ge) show strong interference effects. (Goldsmith 1947).

The mean total cross-section of Ge nuclei for thermal neutrons is about 9×10^{-24} cm², being of the same order of magnitude as that obtained for As.

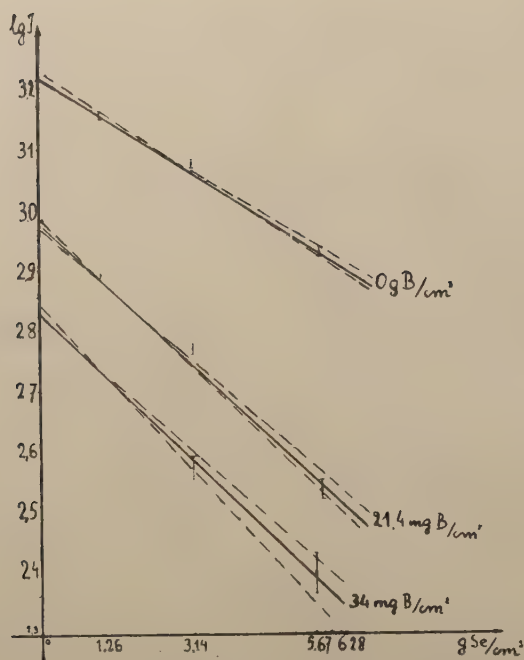


Fig. 4. Absorption curves for Se.

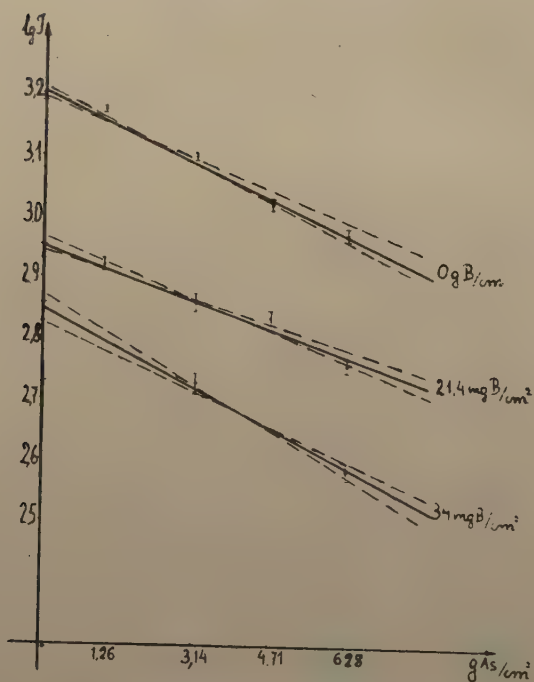


Fig. 5. Absorption curves for As.

Acknowledgements

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THE DEPENDENCE OF THE EFFICIENCY OF GEIGER-MÜLLER COUNTERS FOR GAMMA RAYS UPON THE WALL THICKNESS

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(received July 1, 1950)

This dependence was investigated for brass and lead walls with γ -rays of Ra and MsTh filtered through 2 or 3 cm Pb. The curves of the relative efficiency of the counters versus wall thickness were found to be typical „transition curves“ with flat maxima shifting towards greater thicknesses with increasing energy of the incident photons.

Among the many factors influencing the efficiency of Geiger-Müller counters for γ -rays the counter wall thickness was the least studied one. The γ -rays are recorded in the G.-M. tube through photo-, Compton- and pair-electrons produced in the counter wall by the incident γ -rays. The probability of all these processes increases with increasing wall thickness. However, at the same time the probability of reaching the effective volume of the counter by electrons originating in the outer layers of the walls becomes smaller. This gives rise to a dependence of the relative efficiency for γ -rays upon the thickness of the counter walls.

This dependence was investigated experimentally by Buchmann (1937) on a thin cylindrical Pb counter suspended in a glass vessel. Buchmann changed the wall thickness by covering the counter with a varying number of Pb cylinders. For γ -rays of a RaTh sample filtered through 1,5 cm Pb he found the optimum wall thickness (i. e. that giving the greatest efficiency) to be about 0,65 mm Pb.

Other authors studying the factors influencing the γ -ray counter efficiency (Norling 1941, Bradt and al. 1946) contented themselves with taking always the counter wall thickness not smaller than the range of the most energetic secondary electrons produced by the γ -rays of given energy.

Mme Marty (1947) determined the optimum wall thicknesses for several energies of the γ -rays as the ranges of the fastest secondary electrons. Her data (for a counter with Cu walls) are:

0,2	0,5	1	2	2,5	3,5	5	MeV
0,048	0,195	0,36	0,9	1,2	1,8	2,7	mm

She found also values of the absolute counter efficiency for these γ -energies and remarked that they are valid only in the case when the counter wall thickness is at least as given above. She claimed to have experimentally confirmed her results to within 10%.

The aim of the present work was to examine experimentally how the relative efficiency of brass and lead lined brass G.-M. counters varies with wall thickness, and eventually to find out the optimum wall thickness for γ -rays of given energy. The lack of monoenergetic γ -ray sources has compelled the author to use Ra and Ms Th samples contained in platinum needles (both elements being in equilibrium with their derivatives). The Ra γ -rays were filtered through 2 or 3 cm Pb, the Th γ -rays through 3 cm Pb.

The counters made for the purpose of the present work were 100 mm long and had an inside diameter of 24 mm. They were ordinary cylindrical brass counters except for their bottom which consisted of a foil on which further foils could be placed and pressed by a ring. The foils of the brass counters were of brass 0,1 or 0,22 mm thick those of the lead lined brass counters were of gold (92%), 0,17 mm thick; the latter had their tubes lined inside with a 1 mm thick lead layer.

A channel in lead bricks, 4 \times 5 mm cross section and 30 cm length, collimated the filtered γ -rays on the bottom of the counter parallelly to the counter axis. The measurements consisted in changing the number of foils on the bottom of the counter and registering the number of counts per min corresponding to each thickness. Typical curves of the relative efficiency versus wall thickness are shown in fig. 1 and 2. Starting with some initial wall thickness there is a rapid increase of the efficiency up to a broad and flat maximum. With further increase of the wall thickness the efficiency decreases slowly.

The optimum wall thicknesses were found to be as follows:

For Th γ -rays filtered through 3 cm of lead (main energy 2,62 MeV)

1,1 to 1,2 mm of brass in the brass counter,

0,17 mm Au + 0,7 to 0,8 mm Pb in the lead lined counter.

For Ra γ -rays a pronounced maximum was found only for brass counters. For Ra γ -rays filtered through 3 cm of lead (energy mainly

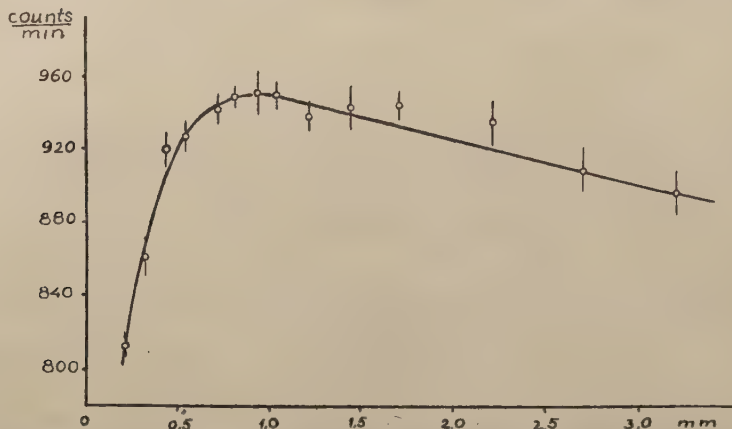


Fig. 1. Relative efficiency versus wall thickness of a brass counter for γ -rays of Th filtered through 2 cm of lead.

in the region 1–2,2 MeV) 0,9 to 1,1 mm of brass. For Ra γ -rays filtered through 2 cm of lead (energy mainly in the region 0,6–2,2 MeV) 0,9 to 1,0 mm of brass.

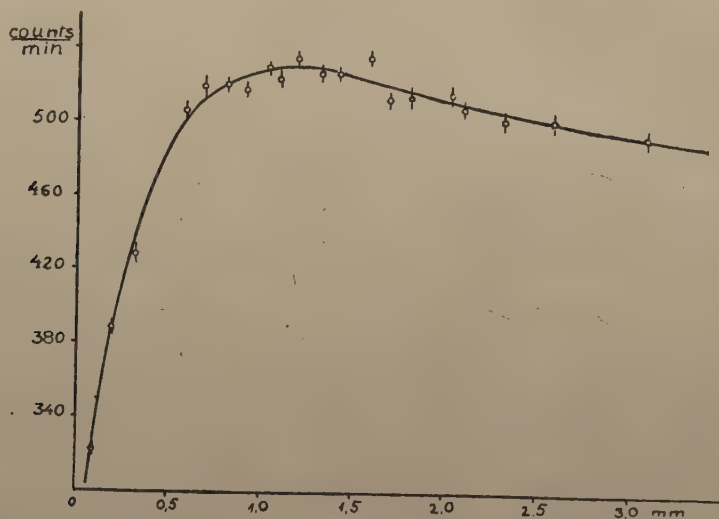


Fig. 2. Relative efficiency versus wall thickness of a brass counter for γ -rays of Ra filtered through 3 cm of lead.

Thus the optimum wall thickness increases with increasing energy of the incident γ -rays.

I wish to express my hearty thanks to Professor H. Niewodniczański for suggesting this problem and for encouragement during the work. I am also very much indebted to Professor M. Mięslowicz and his collaborators for valuable help in preparing the G.-M. counters.

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ON THE LOCAL GAMMA-RADIATION APPEARING IN MEASUREMENTS OF COSMIC RADIATION AT GREAT DEPTHS

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(received August 12, 1950)

The authors give new arguments that the low ionizing isotropic radiation giving more twofold than threefold coincidences in the measurements of cosmic rays at great depths is of local radioactive origin.

The first results of our measurements of the soft, low ionizing radiation at depths up to 660 m w. e. have been recently published (Mięslowicz, Jurkiewicz, Massalski 1950); the present paper contains the results of farther experimental investigations of the same subject. The soft, low ionizing, isotropic radiation was first observed by Barnóthy and Forró (1939) and later discussed by them in several papers (Barnóthy and Forró 1947, 1948, 1950).

In consequence of some discussion caused by our first paper (Barnóthy and Forró 1950, Greisen 1949, 1950), we should like to consider once more the results of Barnóthy and Forró. These authors discovered the radiation under discussion by means of a counter telescope, measuring first twofold and then threefold coincidences. They found that in the circumstances of their measurements at the depth of about 1000 m w. e. the twofold coincidences were 20 times as frequent as the threefold. In their first paper Barnóthy and Forró (1939) admit the possibility of explanation of their results by means of a local γ -radiation. But in their next papers (Barnóthy and Forró 1947, 1948) they exclude this possibility and consider this low ionizing radiation as a component of cosmic radiation. Their chief arguments are:

(1) They consider the ratio of threefold to twofold coincidences as the efficiency of the G. M. counters for this radiation and they evaluate it to 5 per cent. This efficiency is about 10 times higher than the efficiency for the γ -radiation of RaC, which Barnóthy and Forró give as 0,4 per cent.

(2) They have ascertained that this radiation is approximately isotropic, but they have found some maxima on the absorption curve for vertical position of the telescope. The general character of the absorption curve shows that this radiation is absorbed up to 50 per cent by 6 mm Pb; beyond this thickness it is only slightly absorbed and still present at 11 cm Pb. According to Barnóthy and Forró these circumstances exclude the interpretation of this radiation as γ -radiation: they consider it as a low ionizing component of cosmic rays.

Besides the phenomena mentioned above, Barnóthy and Forró describe some other measurements investigated with threefold coincidences which concern the absorption curve and the angular distribution of cosmic radiation at great depths. Independently of the formerly mentioned experiments they conclude from these measurements that perhaps another penetrating low ionizing component of cosmic radiation may exist at those depths. Our paper does not deal with these phenomena but with the radiation formerly described and called A -radiation in our previous paper.

In that paper we separated the A -radiation by simultaneous measurements of threefold and double coincidences. Moreover our counter telescope differed from that of Barnóthy and Forró, as it was protected against side showers by means of anti-coincidence counters. We analysed the problem of the efficiency of the counters for A -radiation and we ascertained that it was impossible to consider the ratio of the threefold to twofold coincidences as the efficiency of the counters because of the presence of an appreciable number of ionizing particles. By comparison of the A -component with the radiation absorbed by 50 mm Pb, measured with a single counter (where the ionizing component is only a very small fraction of the whole radiation), we have obtained as the efficiency of the twofold telescope the expression $\lambda\lambda'$, λ being the efficiency of the single counter for that radiation and λ' the probability that a particle or a γ -photon which has entered the first counter in the solid angle of the telescope and discharged it will also discharge the second counter. We have obtained for λ' the value of 0,002 which is about 20 times smaller than that given by Barnóthy and Forró. This value is several times smaller than the efficiency of a single counter for γ -radiation. The preliminary results of our absorption measurements did not confirm the anomaly of the absorption found by Barnóthy and Forró. For the absorption coefficient we obtained approximately the same value as for γ -radiation of about 1 MeV energy.

These results, together with the isotropy of the radiation, brought us to the conclusion that it is very possible that we have here to do

with a γ -radiation of local radioactive origin, contrary to the opinion of Barnóthy and Forró expressed in their recent papers (1947, 1948).

As the results of our later measurements we are now able to present definite evidence confirming our conclusion that the A -radiation is of local radioactive origin. We think that this explanation may throw some additional light on the opinion of Greisen (1950) on this subject.

Measurements of the A -radiation at different depths and at the same depth in different places

The intensity of the A -radiation was measured at different depths and different places and compared

(1) with the intensity of cosmic radiation by means of threefold coincidences, and

(2) with the intensity of the radiation measured with a single counter.

At a certain depth we found two places, differing in their geological characteristics, with very different local γ -ray intensities. The results of our measurements are given in Table I. T is the number of threefold

Table I

Depths m. w. e.	Surroundings	T p. h.	D p. h.	$A=D-T$ p. h.	N p. m.
145	silt	$42,2 \pm 0,5$	$45,3 \pm 0,5$	$3,1 \pm 0,15$	$301 \pm 5,5$
220	rock-salt	$16,3 \pm 0,5$	$17,1 \pm 0,5$	$0,8 \pm 0,1$	$83 \pm 5,5$
313	rock-salt	$8,5 \pm 0,4$	$10,2 \pm 0,4$	$1,7 \pm 0,2$	153 ± 6
313	silt	$8,2 \pm 0,4$	$14,3 \pm 0,5$	$6,1 \pm 0,3$	$543 \pm 4,5$
415	rock-salt	$3,78 \pm 0,3$	$4,65 \pm 0,2$	$0,87 \pm 0,1$	99 ± 3
545	rock-salt	$1,94 \pm 0,07$	$2,70 \pm 0,09$	$0,76 \pm 0,05$	$82 \pm 3,6$
660	rock-salt	$1,38 \pm 0,06$	$1,91 \pm 0,07$	$0,53 \pm 0,04$	51 ± 3

coincidences p. h., i. e., the intensity of the ionizing component of cosmic radiation; D is the number of double coincidences; $A=D-T$ is the number of coincidences caused by the A -radiation; N is the number of pulses in the single counter p. m. obtained by subtracting from the number of pulses in this counter the background of the counter (12 pulses p. m.) as well as the number of pulses caused by the ionizing component of cosmic radiation. In most cases this last number is quite small and may be neglected.

The dimensions of our telescope were the same as those given in our first paper (the distance between the extreme counters was 18 cm, the areas of the counters were $4,3 \times 65 \text{ cm}^2$). The single counter

used in these experiments was of the same size as the extreme counters of the telescope. The wall thickness of all counters was 1 mm.

It may be seen from these results that the dependence of the intensity T of cosmic radiation on the depth H for depths of 220–660 m w. e. follows the simple law $T \sim H^{-\gamma}$, in agreement with the earlier measurements of different authors (e. g. Clay and Gemert 1939). On the diagram $\log T$ vs. $\log H$ appears an almost straight line with a coefficient $\gamma = 2.4$. We have found no dependence of the number of A -coincidences upon the number of T coincidences, i. e. upon the intensity of the cosmic radiation. On the other hand, we see that the A -radiation is, within the limits of experimental errors, proportional to N . N does not depend upon the depth but is connected with the geological structure of the layers in the surroundings of the apparatus. As is well known, the radioactive contents in rock-salt are very low in general, but in silt they are relatively high. This can be seen from Table I for two places at 313 m w. e., 15 m distant from each other. One of these places is surrounded by silt, the other one by rock-salt. Taking all this into consideration, we assume the number N to be the measure of the γ -radiation of the surroundings. We see that for the above mentioned two places we have also two different values for A which are proportional to N , i. e. to the intensity of the local γ -radiation, and independent of the cosmic ray intensity.

We present this fact as the main argument in our demonstration that the A -radiation is the local γ -radiation having its source in radioactive contaminations of the surroundings.

Our measurements of the absorption of the A -radiation enabled us also to determine the character of the radiation concerned. Fig. 1 gives the results of our new, more accurate measurements of the absorption of the A -radiation for the thicknesses of 0–20 mm Pb.

Discussion of results

We consider our results as the definitive proof that the A -radiation is of local radioactive origin. After the publication of our previous paper, Barnóthy and Forró (1950)¹ have given some results which might be also considered as a proof of the local γ -ray character of the A -radiation. In particular, the differences between our measurements and those of Barnóthy and Forró at 1000 m w. e. carried out in a corridor covered on all sides with bricks (which are much more

¹ We are greatly indebted to Professor Barnóthy for sending us a copy of his report at the Midwest Cosmic Ray Group Meeting, Ann Arbor 1950.

radioactive than rock-salt) are now clear. Another proof of the correctness of our interpretation may be found in the results obtained by Barnóthy and Forró in a coal mine at 730 m w. e.: low intensity of local radioactivity and low intensity of A -radiation. Also the efficiency of their counters which they have evaluated now according to our method is of the same order of magnitude as in our case.

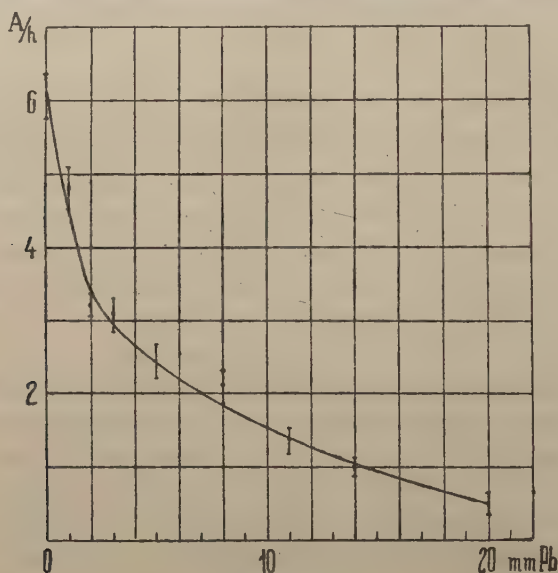


Fig. 1.

We cannot explain the existence of the maxima at 6 mm Pb found by Barnóthy and Forró in the absorption curve of the radiation giving double coincidences. We have found no indication of that maximum, though it seems to us that we had more advantageous conditions for its discovery, notwithstanding the fact that we worked at smaller depths. By simultaneous recording of double and threefold coincidences we were able to diminish the statistical error of the difference $D - T$ which is the measure of the low ionizing radiation; furthermore we had a smaller background-rate of A -radiation and a higher intensity of cosmic rays (at 313 m w. e.) which ought to be responsible for this maximum.

Indeed the mechanism of the twofold coincidences given in appreciable amount by single γ -photons has to be explained. Retaining the conception advanced in our first paper, we suggest that a γ -photon entering the first counter may be scattered there in a Compton process and after discharging this counter may be recorded afterwards in the second counter. In our circumstances these rare double processes occur

at the rate of several coincidences per hour and it is possible to observe them owing to the very low intensity of cosmic rays underground. It is obvious that the efficiency for γ -rays of a counter in coincidences is lower than the efficiency of a single counter. This is so because of the diminution of the energy of the γ -photon in the first Compton process and because of the fact that the double coincidences are not possible if the first counter is operated through some other process than the Compton effect.

We must distinguish the case of the isotropic radiation underground from the case of a point source of radiation placed in the plane of the telescope, as considered by Barnóthy and Forró in their recent paper (1950). In the first case we get from our last measurements for λ' the value 0,004 which is a quite reasonable value for natural radioactivity if we take into account the reduction of energy in the Compton processes. In the second case the value of λ' must be much lower due to scattering, which produces an effective decrease of the efficiency in addition to all the causes already mentioned. It is true that in the case of isotropic radiation some γ -rays leave the solid angle of the telescope due to scattering but others enter it in approximately the same amount. The problem of the mechanism of the coincidences produced by γ -photons in two counters is the subject of further investigation now being carried out in our Laboratory.

This work has been performed under the auspices of the Cosmic Ray Commission of the Polish Academy of Science and Letters.

Note added in proof. Recently we came across an abstract of a paper of Bollinger (1950) who investigated the excess of twofold over threefold coincidences at great depths and came to the same conclusion that it is caused by a local γ -radiation.

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ON THE RANGE-ENERGY RELATION OF LOW ENERGY PROTONS AND α PARTICLES IN A PHOTOGRAPHIC EMULSION

by Ludwik NATANSON, Institute of Experimental Physics, University of Warsaw

(received August 22, 1950)

The lengths of tracks of tritons and α -particles produced in the reaction $\text{Li}^6(n, \alpha)\text{H}^3$ have been measured in Ilford „Nuclear Research“ emulsion C2, and the results of these measurements have been compared to those values which should be expected from Rotblat's range-energy curves.

The relationship between the energy of a particle and its range in a medium in which it can be directly measured, as in a cloud chamber or in a photographic emulsion, may provide a basis for the evaluation of energies in investigations of nuclear phenomena or of cosmic radiation. On the other hand, it may also give some useful information on the interaction between a particle and the electrons and nuclei of the medium.

By measuring the track lengths of particles scattered elastically through various angles by a homogenous beam of deuterons, Rotblat (1950) determined the ranges of protons and α -particles in the Ilford „Nuclear Research“ emulsion C2 for energies up to about 8 MeV.

Since the Q value for the nuclear reaction

$$\text{Li}^6(n, \alpha)\text{H}^3$$

is now known from other experiments with a comparatively high degree of accuracy, it seemed interesting to measure once more the lengths of tracks of tritons and α -particles produced in this reaction and to compare the results of these measurements to those values which should be expected from Rotblat's range-energy curves.

According to recent accurate measurements by Tollestrup, Fowler and Lauritsen (1949) the energy release in the $\text{Li}^6(n, \alpha)\text{H}^3$ reaction is

$$Q = 4.788 \pm 0.023 \text{ MeV.}$$

Dividing this amount between the two particles in inverse ratio to their masses we get

$$Q_{\alpha} = 2.057 \text{ MeV}, \quad Q_{\text{triton}} = 2.731 \text{ MeV}.$$

Making use of Rotblat's curve for α -particles we find the range of a 2.057 MeV α -particle:

$$R'_{\alpha} = 7.05 \mu$$

or, if we take into account the $+3\%$ correction for moisture in the emulsion,

$$R_{\alpha} = 7.26 \mu.$$

It follows from theoretical considerations that, when the velocity of an incident ionizing particle is high compared to the orbital velocities of the electrons in the stopping medium, its range may be expressed in the form

$$R = Mf(V_0)/e^2,$$

where M is the mass of the particle, e its charge and V_0 its initial velocity. Hence the ranges of particles differing in mass but carrying the same charge and having the same initial velocities should be directly proportional to the masses.

Insofar as the above formula is correct, it is thus possible to find the range of a triton on the basis of a range-energy curve for protons. The triton range for any given energy should be k times greater than that of a proton of k times smaller energy, k being the mass ratio:

$$k = \text{triton mass/proton mass}.$$

Applying this usual method to the case of a 2.73 MeV triton we find from Rotblat's range-energy curve for protons, after correction for the moisture content in the emulsion, a range:

$$R_{\text{triton}} = 38.9.$$

Our experimental procedure may be briefly described as follows. A lithium loaded C2 plate was irradiated with neutrons from a Be+40 mg *Ra* source through a thick Pb screen to absorb γ -radiation. The whole was covered with large blocks of paraffin. In view of the difficulty of locating exactly the point where a disintegration occurs, no attempt was made to measure the α and the triton tracks separately and only sums of both tracks were measured. Only well-defined tracks, ending within the emulsion and having the appearance of a single straight line, were selected for measurement. All tracks either forming an angle visibly differing from 180° due to the residual momentum of a noncompletely thermalized neutron, or having an angle of dip over 15° , were eliminated.

The measurements were effected on a Spencer microscope with an oil immersion $95\times$ object glass and a Baker micrometer eyepiece with a movable cobweb actuated by a micrometetr screw. The latter had been previously calibrated on a standard micrometer scale — 1 mm divided in 100 parts — placed on the microscope stage. One division of the drum was found to correspond to a $0.931\ \mu$ shift of the cobweb. The differences in depth between the ends of an α and a proton track were measured with the micrometer screw for fine focus adjustment and the component perpendicular to the plane of the plate was multiplied by the factor 2.2 to compensate for the shrinkage of the emulsion.

In all, 40 tracks were measured, each component perpendicular to the plane of the plate being measured three, and each component parallel to the plane of the plate being measured five, times. The mean value obtained is

$$R_{\text{total}} = R_{\alpha} + R_{\text{triton}} = 42.67\ \mu$$

with a mean square root deviation

$$\pm 0.27\ \mu.$$

Again using Rotblat's curves to find energies corresponding to ranges which, added together, would give the above value of R_{total} and would have the correct ratio to one another, we get;

$$E_{\alpha} = 1.94\ \text{MeV}, \quad E_{\text{triton}} = 2.58\ \text{MeV}$$

and thus

$$Q = 4.52\ \text{MeV}.$$

The wide discrepancy between this value and that found by Tollestrup, Fowler and Lauritsen, using more accurate methods, lends support to the view that track lengths measured on different instruments and in different laboratories are not strictly comparable. For higher precision work it would probably be preferable if the average length of a track associated with some easily obtainable nuclear event were adopted as standard of reference.

However, it should be noted that the value of R_{total} as found by us is in excellent agreement with that given by Mme Faraggi (1948)

$$R_{\text{total}} = 43.0 \pm 0.4\ \mu.$$

She has determined the ranges of the two products of the disintegration of Li^6 by thermal neutrons separately, but the degree of uncertainty of these determinations must be higher than that of their sum.

Keepin and Roberts (1949), working on plates of a different type, and with fast neutrons, got a somewhat higher value:

$$R_{\text{total}} = 45.0 \pm 1.7 \mu$$

but Cüer, Longchamp, Combes and Gorodetzky (1949) who have measured R_{triton} only, give:

$$R_{\text{triton}} = 35.46 \pm 0.2 \mu.$$

If we subtract the latter value from our own R_{total} there remains for R_{α} almost exactly what should be expected from the Q value of Tollestrup, Fowler and Lauritsen and from Rotblat's curve for α particles.

This may be taken as an indication that Rotblat's curve for α -particles is reliable down to energies about 2 MeV, whereas the curve for protons should run some 30 KeV higher in the region about 12μ .

In the region of still lower energies, Cüer and Morand measured the range of 0.56 MeV protons from the reaction

$$N^{14}(n, p)C^{14}$$

and so determined another point on the range-energy curve lying also slightly above Rotblat's curve in this region.

It would probably be possible to draw a smooth curve passing through both these points (i. e. 0.56 MeV — 6μ and 0.91 MeV — 11.5μ , the ranges being taken for a dry emulsion) and joining Rotblat's curve about 1 MeV.

The stopping power, relative to normal air, of the C2 lithium loaded emulsion as computed from Cüer's, Longchamp's, Combes's, Gorodetzky's and from our own experimental data would be (assuming average humidity condition of the plates):

for protons about 0.9 MeV approx. 1880,
for α particles about 2 MeV approx. 1430.

I am indebted to Professor Pieńkowski for this interest in this work and for his helpful advice.

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THE NEW EINSTEIN THEORY AND THE EQUATIONS OF MOTION

by L. INFELD, Universities of Toronto and Warsaw

(received Sept. 10, 1950)

It is known that the field equations of General Relativity Theory determine motion without any additional equations. If, besides the gravitational field, we assume the electromagnetic field, then we obtain the Lorentz equations of motion. The question is what kind of equations of motion we obtain in Einstein's new theory. The answer is: we do not obtain the Lorentz equations of motion by means of the new approximation method; the equations of motion are essentially the same as in General Relativity Theory, if an electromagnetic field is absent.

1. Introduction

The new Einstein theory (1950) is mathematically attractive but its role in science can only be established through the conclusions that can be drawn from it. Einstein himself hopes that his new theory will turn out to be a real field theory, that is, he believes that his equations possess solutions free from singularities and representing particles. To show that such solutions exist (or that they do not) is a difficult task. The one formulated in this paper is a more modest one: to investigate whether the new Einstein theory gives equations of motion which are consistent with experience, that is, whether we can obtain the Lorentz equations of motion. Unfortunately the result is negative; the equations of motion remain Newtonian and are uninfluenced by the „electromagnetic field“.

Yet it would not be right to regard this result as a death blow to Einstein's theory. The conclusion drawn here and the argument given follow along conventional lines as far as the electromagnetic field is concerned. It is possible that not Einstein's theory, but rather the conventional approach is at fault.

In a series of papers (Einstein 1938, 1940, 1949; Infeld 1938, 1940) the problem of motion, as determined by the field equations alone, was investigated according to General Relativity Theory. Here we apply essentially the same method to Einstein's new theory. Knowledge of the earlier papers is assumed, especially in the content of section 3 and 4.

2. Components of the affine connection

In the new Einstein theory, we have two kinds of differentiation: one with a + sign and one with a - sign. Changing Einstein's notation slightly and writing the \pm sign under the stroke to denote covariant differentiation we have

$$A_{\pm k}^s = A_{,k}^s + A^p \Gamma_{pk}^s, \quad A_{\pm k}^s = A_{,k}^s + A^p \Gamma_{kp}^s \quad (2.1)$$

where comma denotes ordinary differentiation. Similarly we have

$$A_{\pm k}^s = A_{,k}^s - A_p \Gamma_{sk}^p, \quad A_{\pm k}^s = A_{,k}^s - A_p \Gamma_{ks}^p. \quad (2.2)$$

The fundamental tensor g_{ik} has its symmetric and antisymmetric parts. The components of the affine connection (Γ_{kl}^s) are defined through algebraic equations which state that the covariant \pm differentiation of this tensor vanishes. More explicitly we have

$$g_{ik \pm l} = g_{ik,l} - g_{sk} \Gamma_{il}^s - g_{is} \Gamma_{lk}^s = 0. \quad (2.3)$$

These are 64 equations for the calculation of the 64 Γ_{kl}^s components. To these Einstein adds the condition

$$\Gamma_k = 2(\Gamma_{ks}^s - \Gamma_{sk}^s) = 0. \quad (2.4)$$

These are complicated algebraic equations. But, as we shall see later, when investigating the equations of motion we need only approximate solutions of (2.3) and (2.4). Therefore, we shall solve them only approximately. But our procedure will show that we can push the approximation as far as we wish. We write

$$g_{ik} = a_{ik} + f_{ik} \quad (2.5)$$

where a_{ik} is the symmetric and f_{ik} the antisymmetric part of g_{ik} . In this paper we shall speak only about the covariant f_{ik} . But as far as the a_{ik} are concerned, we can and shall define a^{ls} by means of

$$a_{ks} a^{sl} = \delta_k^l. \quad (2.6)$$

But we must bear in mind that a^{ls} defined by (2.6) is *not* the symmetric part of g^{ls} defined by means of

$$g_{sk} g^{sl} = \delta_k^l. \quad (2.7)$$

Instead of starting with (2.5) we could have started with a division of the contravariant tensor g^{kl} into symmetric and antisymmetric parts

$$g^{kl} = a^{kl} + \varphi^{kl}.$$

Our entire argument would have been different, though very similar, and the conclusions, of course, the same as reached in this paper.

Thus when we use the Christoffel symbols [] and { }; we shall understand them as those referring to a_{kl} :

$$[kl, s] = \frac{1}{2}(a_{ks, l} + a_{ls, k} - a_{kl, s}), \quad \left\{ \begin{matrix} p \\ kl \end{matrix} \right\} = a^{ps}[kl, s], \quad (2.8)$$

where a^{ps} is defined by means of (2.6), and *not* as the symmetric part of g^{ps} . We shall now write

$$\Gamma_{il}^s = \left\{ \begin{matrix} s \\ il \end{matrix} \right\} + M_{il}^s \quad (2.9)$$

and, therefore, the problem of finding the Γ 's is reduced to that of finding the M 's.

One more notation: we shall introduce ordinary covariant Riemannian differentiation:

$$A_{k, l} = A_{k, l} - A_s \left\{ \begin{matrix} s \\ kl \end{matrix} \right\} \text{ etc.} \quad (2.10)$$

If we take into account (2.5) and (2.9), then we can write equation (2.3), which defines the Γ 's, in the following form

$$f_{ik, l} - a_{sk} M_{il}^s - a_{is} M_{kl}^s - f_{sk} \left\{ \begin{matrix} s \\ il \end{matrix} \right\} - f_{is} \left\{ \begin{matrix} s \\ lk \end{matrix} \right\} - f_{sk} M_{il}^s - f_{is} M_{lk}^s = 0. \quad (2.11)$$

This is so, because

$$a_{kl, s} = 0. \quad (2.12)$$

Or, (2.11) can also be written in the slightly simpler form:

$$f_{kl, i} - a_{sl} M_{ki}^s - a_{ks} M_{il}^s - f_{sl} M_{ki}^s - f_{ks} M_{il}^s = 0. \quad (2.13)$$

We now write two equations, by changing the indices in (2.13):

$$f_{li, k} - a_{sl} M_{lk}^s - a_{ls} M_{kl}^s - f_{sl} M_{lk}^s - f_{ls} M_{kl}^s = 0, \quad (2.14)$$

$$f_{kl, i} - a_{sl} M_{ki}^s - a_{ks} M_{il}^s - f_{sl} M_{ki}^s - f_{ks} M_{il}^s = 0. \quad (2.15)$$

Now, if we form (2.13) - (2.14) + (2.15), we have

$$\frac{1}{2}(f_{ik, l} + f_{kl, i} - f_{li, k}) - a_{ks} M_{il}^s - f_{is} M_{lk}^s - f_{sl} M_{ki}^s = 0. \quad (2.16)$$

We define

$$I_{ikl} = \frac{1}{2}(f_{ik, l} + f_{kl, i} + f_{li, k}) = \frac{1}{2}(f_{ik, l} + f_{kl, i} + f_{li, k}) \quad (2.17)$$

and we have

$$a_{ks} M_{il}^s = f_{li, k} - I_{ilk} - f_{is} M_{lk}^s - f_{sl} M_{ki}^s, \quad (2.18)$$

or

$$M_{il}^p = a^{kp}(f_{li, k} - I_{ilk} - f_{is} M_{lk}^s - f_{sl} M_{ki}^s). \quad (2.19)$$

Let us now write

$$a_{ks} = \eta_{ks} + h_{ks}, \quad (2.20)$$

where $\eta_{00} = 1$, $\eta_{11} = \eta_{22} = \eta_{33} = -1$ and $\eta_{kl} = 0$ for $k \neq l$. Assuming that h_{ks} , f_{ks} , M_{kl}^s are all of the same order, we can solve (2.14) by successive approximation, crossing out in the first approximation the terms which contain M 's on the right-hand side of (2.19) because they are multiplied by f 's. Then we can introduce again on the right-hand side of (2.19), the first approximation of M and obtain M up to the second approximation, and so on. Thus (2.19) can be used to find the M 's up to an arbitrary approximation.

3. The M 's according to the new approximation method

We shall now use what we called (Einstein 1938) the „new approximation method“ for calculating the M 's. Thus from now on we change our notation in the following respect: all indices run from 1 to 3 and not, as before, from 0 to 3. The method itself distinguishes time and assumes that the derivatives with respect to time are small compared with those with respect to space.

When investigating the problem of motion, we developed the gravitational field into a power series in the parameter λ :

$$\begin{aligned} g_{00} &= 1 + \lambda^2 g_{00}^{(2)} + \lambda^4 g_{00}^{(4)} + \dots \\ g_{0m} &= \lambda g_{0m}^{(3)} + \lambda^5 g_{0m}^{(5)} + \dots \\ g_{mn} &= -\delta_{mn} + \lambda^2 g_{mn}^{(2)} + \lambda^4 g_{mn}^{(4)} + \dots \end{aligned} \quad (3.1)$$

We shall assume the same development here for nonsymmetric g 's. Thus we have

$$\begin{aligned} a_{00} &= 1 + \lambda^2 a_{00}^{(2)} + \lambda^4 a_{00}^{(4)} + \dots \\ a_{nm} &= \lambda^3 a_{nm}^{(3)} + \lambda^5 a_{nm}^{(5)} + \dots \\ a_{mn} &= -\delta_{mn} + \lambda^2 a_{mn}^{(2)} + \lambda^4 a_{mn}^{(4)} + \dots \end{aligned} \quad (3.2)$$

and

$$\begin{aligned} f_{0l} &= \lambda^3 f_{0l}^{(3)} + \lambda^5 f_{0l}^{(5)} + \dots \\ f_{mn} &= \lambda^2 f_{mn}^{(2)} + \lambda^4 f_{mn}^{(4)} + \dots \end{aligned} \quad (3.3)$$

(We may remark in passing that this development in λ 's, which puts the a 's and f 's on an equal footing, is not the only possible one, though it is the simplest. The final result would be the same if we were to regard the order of f_{0l} even and that of f_{mn} odd.).

Let us now go back to (2.19) and calculate the M 's. We have

$$\begin{aligned} M_{00}^0 &= 0, & M_{00}^s &= M_{0m}^0 = M_{m0}^0 = 0. \\ M_{0s}^t &= -f_{0s,t} + I_{0st}, & M_{st}^0 &= f_{st,0} + I_{st0}, & M_{mn}^p &= -f_{mn,p} + I_{mnp}. \end{aligned} \quad (3.4)$$

But for the equations of motion we need the Γ 's at least up to the fourth order. Only M 's with even zeros can be of this order. Thus if we introduce (3.4) into the right-hand side of (2.19), we obtain

$$\begin{aligned} M_{00}^s &= 0, & M_{0l}^0 &= f_{0l,0} \\ M_{mn}^p &= -f_{mn,p} + I_{mnp} - f_{ms}(-f_{np,s} + I_{nps}) \\ &\quad - f_{sn}(-f_{pm,s} + I_{pms}) + a^{kp}(f_{mn,k} - I_{mnk}) - f_{ms}\left\{\begin{matrix} s \\ pn \end{matrix}\right\} - f_{sn}\left\{\begin{matrix} s \\ mp \end{matrix}\right\}. \end{aligned} \quad (3.5)$$

Let us note that with the exception of M_{mn}^p all the other M 's are antisymmetric in the lower indices. For future reference, we shall write down the symmetric and antisymmetric parts of M_{mn}^p . Following Einstein's notation, we shall denote them by

$$M_{\underline{mn}}^p \quad \text{and} \quad M_{\overline{mn}}^p$$

respectively. Then:

$$\begin{aligned} M_{\underline{mn}}^p &= -f_{ms}(-f_{np,s} + I_{nps}) - f_{sn}(-f_{pm,s} + I_{pms}) \\ M_{\overline{mn}}^p &= -f_{mn,p} + I_{mnp} + a^{kp}(f_{mn,k} - I_{mnk}) \\ &\quad - f_{ms}\left\{\begin{matrix} s \\ pn \end{matrix}\right\} - f_{sn}\left\{\begin{matrix} s \\ mp \end{matrix}\right\}. \end{aligned} \quad (3.6)$$

Thus everything is prepared for finding the equations of motion.

4. The field equations of the second order

We denote the contracted curvature tensor by R_{kl} . We rewrite equations (15) and (24) of Einstein's paper (1950):

$$R_{kl} = \Gamma_{kl,s}^s - \Gamma_{kt}^s \Gamma_{sl}^t - \frac{1}{2}(\Gamma_{ks,l}^s + \Gamma_{ls,k}^s I + \Gamma_{kl}^s \Gamma_{st}^t) = 0, \quad (4.1)$$

where in this case *exceptionally* all the indices run again from 0 to 3. Now we shall denote by P_{kl} ($k, l = 0, 1, 2, 3$) the Riemannian curvature

tensor which can be gained from (4.1) by introducing the Christoffel symbols of the second kind instead of the Γ 's. If we return to our notation in which the indices run from 1 to 3, we have, because of (4.1), (3.4) and (2.9)

$$R_{00} = P_{00}, \quad R_{0m} = P_{0m} - f_{0m,ss} + I_{0ms,s}, \quad R_{mn} = P_{mn} - f_{mn,pp} + I_{mnp,p}. \quad (4.2)$$

Thus from (4.2) follows

$$R_{00} = P_{00} = 0, \quad R_{0m} = P_{0m} = 0, \quad R_{mn} = P_{mn} = 0, \quad (4.3)$$

and:

$$-f_{0m,ss} + I_{0ms,s} = 0, \quad -f_{mn,pp} + I_{mnp,p} = 0. \quad (4.4)$$

To these equations we must add (2.4):

$$\Gamma_k = \frac{1}{2}(\Gamma_{ks}^s - \Gamma_{sk}^s) = M_{ks}^s = -f_{ms,s} = 0, \quad \Gamma_0 = M_{0s}^s = -f_{0s,s} = 0 \quad (4.5)$$

Thus (4.4) and (4.5) lead to the following field equations because of (2.17)

$$f_{mn,ss} = 0, \quad f_{ms,s} = 0, \quad f_{0m,ss} = 0, \quad f_{0s,s} = 0. \quad (4.6)$$

We see that in the second approximation the equations split into equations of the „gravitational“ and „electromagnetic“ fields.

Of course, these conclusions have no meaning near the „center“ of the particle since there the fields are strong and there is no justification for an approximation procedure. Indeed (4.5) and (4.6) admit only a solution with a singularity and can only be valid far from the „center“, where the field is weak. Thus we can imagine a sphere around the particle and regard the solutions of (4.6) as representing the field outside this sphere. But the entire technique of finding equations of motion is based on the formation of such spheres, on the formation of surfaces around the particles and the proof that some surface integrals do not depend on the size and shape of the surface as long as each of them encloses only one particle. Thus if the particles are not vary near to each other, the deduced equations of motion which represent the motion of singularities will be the same as those of particles with regular solutions (if they exist).

We turn now to equations (4.5) to look for a solution that can be identified, far from the centers, with a field of p charges.

We introduce

$$\varphi = \varphi_2^1 + \varphi_2^2 + \varphi_2^3 + \dots + \varphi_2^p \quad (4.7)$$

where φ_2^k corresponds to the k -th particle. Its path is described by three functions of time:

$$\xi_2^k(\tau) \quad (4.8)$$

and velocities of order λ , accelerations of order λ^2 by

$$\dot{\xi}_2^k(\tau) \quad \text{and} \quad \ddot{\xi}_2^k(\tau) \quad (4.9)$$

respectively. Furthermore we denote by r^k the distance of the point in space from the k -th path at a certain given moment:

$$r^2 = (x^m - \xi_2^m)(x^m - \xi_2^m). \quad (4.10)$$

Using the notation familiar to those who have studied the quoted papers (Einstein 1938, 1940, 1949; Infeld 1938, 1940), we have

$$\varphi_2^k = e_2^k (r^k)^{-1}, \quad (4.11)$$

where e_2^k is proportional to the charge.

Now we define:

$$f_{mn} = \varepsilon_{mns} \varphi_{,s} \quad (4.12)$$

and we see that indeed the equations

$$f_{mn,ss} = 0; \quad f_{ms,s} = 0 \quad (4.13)$$

are satisfied. The first one is satisfied because f_{mn} is a harmonic function; the second because ε_{mns} is a completely antisymmetric Cartesian tensor in three dimensions.

To satisfy the other two equations, we introduce

$$\varphi_m = \sum_{k=1}^p \varphi_m^k; \quad \varphi_m = \varphi_2^k \xi_2^m \quad (4.14)$$

and

$$f_{0t} = \varepsilon_{0tnm} \varphi_{n,m}$$

where ε_{0tnm} are components of a completely antisymmetrical Cartesian tensor in four dimensions. Again we see that the equations

$$f_{0m,ss} = 0; \quad f_{s0,s} = 0$$

are satisfied because f_{0m} is a harmonic function and ε_{0nm} is completely antisymmetric.

To this solution we have to add the solution of the gravitational field. This however can be omitted since this problem was carefully investigated in previous papers (Einstein 1938, 1940, 1949; Infeld 1938, 1940).

5. The equations of motion

The theory of deducing equations of motion from field equations is not simple. In the case of General Relativity Theory, we can show that field equations can be satisfied only in the fourth order if the singularities (representing particles) move according to Newtonian law. But our question here is: what changes are induced (in the fourth approximation) by the additional terms, that is, by the fact that g_{kl} is not symmetric. Here we shall only give the method. Its justification is clear to anyone who has studied the quoted papers.

Let us form

$$-A'_{mn} = (R_{mn} - P_{mn}) - \frac{1}{2} \delta_{mn} (R_{00} - P_{00}) - \frac{1}{2} \delta_{mn} (R_{ss} - P_{ss}). \quad (5.1)$$

After finding A'_{mn} , we form a surface surrounding the k -th electric singularity which, according to our results, may be, but need not be a gravitational singularity as well. (This is so because the two fields do not mix in the second approximation). Denoting by n_k the „normal unit“ vector to the surface, that is

$$n_k = \cos \vec{(n, x^k)}, \quad (5.2)$$

we form

$$\frac{1}{4\pi} \int_4^k 2 A'_{mk} n_k dS = C_m^k, \quad (5.3)$$

the integral to be taken over the surface surrounding the k -th singularity. If

$$A'_{mk,k} = 0,$$

the integral in (5.3) will not depend on the shape of the surface. But then it can depend only on the ξ 's and their time derivatives, thus giving a contribution to the equations of motion.

The theorem is obvious to anyone who has studied the problem of motion as developed in (Einstein 1938, 1940, 1949; Infeld 1938, 1940).

Thus to form A'_{mn} we must calculate $R_{00} - P_{00}$ and $R_{mn} - P_{mn}$. The definition (4.1), together with (3.4) and (3.5) result in

$$R_{00} - P_{00} = 0. \quad (5.4)$$

As a result of (4.1), (3.4) and (3.6), a straightforward calculation gives

$$\begin{aligned} P_{mn} - R_{mn} = & \left\{ -\frac{f_{ms}}{2} \left(-\frac{f_{np,s}}{2} + \frac{I_{nps}}{2} \right) - \frac{f_{sn}}{2} \left(-\frac{f_{pm,s}}{2} + \frac{I_{pms}}{2} \right) \right\}_{,p} \\ & - \frac{1}{2} \left\{ -\left[\frac{f_{st}}{2} \left(-\frac{f_{tm,s}}{2} + \frac{I_{tms}}{2} \right) \right]_{,n} - \left[\frac{f_{ts}}{2} \left(-\frac{f_{nt,s}}{2} + \frac{I_{tps}}{2} \right) \right]_{,m} \right. \\ & \left. - \left(-\frac{f_{mt,s}}{2} + \frac{I_{mts}}{2} \right) \left(-\frac{f_{sn,t}}{2} + \frac{I_{snt}}{2} \right) \right\}. \end{aligned} \quad (5.5)$$

Many of these expressions vanish because of the field equations (4.6) and (4.12). For example, the tensor I_{mnp} has only one independent component different from zero. Calculating I_{123} , we find from (4.12) and (2.17)

$$I_{123} = \frac{1}{2} \Delta \varphi = 0. \quad (5.6)$$

Thus we can cross out in (5.5) all expressions containing I . The expression $\frac{f_{st}}{2} \frac{f_{tm,s}}{2}$ appearing in (5.5) can be written

$$\left. \begin{aligned} \frac{f_{st}}{2} \frac{f_{tm,s}}{2} &= \varepsilon_{str} \varepsilon_{tmp} \varphi_{,r} \varphi_{,ps} \\ &= -(\delta_{sm} \delta_{rp} - \delta_{sp} \delta_{rm}) \varphi_{,r} \varphi_{,ps} = -\varphi_{,p} \varphi_{,pm}. \end{aligned} \right\} \quad (5.7)$$

Therefore

$$\left. \begin{aligned} R_{mn} - P_{mn} &= \varphi_{,pn} \varphi_{,pm} + \varphi_{,p} \varphi_{,pmn} + \frac{f_{ms,p}}{2} \frac{f_{np,s}}{2} \\ R_{ss} - P_{ss} &= \varphi_{,ps} \varphi_{,ps} + \frac{f_{ts,p}}{2} \frac{f_{tp,s}}{2} = 2\varphi_{,ps} \varphi_{,ps}. \end{aligned} \right\} \quad (5.8)$$

From (5.4) and (5.8) we can now find Λ'_{mn} defined in (5.1):

$$-\Lambda'_{mn} = \left\{ \frac{f_{ms}}{2} \frac{f_{np,s}}{2} + \delta_{pn} \varphi_{,rn} \varphi_{,r} - \delta_{mn} \varphi_{,pr} \varphi_{,r} \right\}_{,p}. \quad (5.9)$$

But the expression inside the brackets is antisymmetric in the indices (np) . We see also that

$$\Lambda'_{mn,n} = 0. \quad (5.10)$$

Thus the surface integral $\int 2\Lambda'_{mk} n_k dS$ does not depend on the shape of the surface. Instead of (5.9) we write

$$-\Lambda'_{mn} = F_{mnp,p}$$

where F_{mnp} is the expression in the brackets of (5.9) satisfying the conditions

$$F_{mnp} = -F_{mpn}, \quad F_{mnp,pn} = 0. \quad (5.11)$$

Thus we have to evaluate the surface integral

$$\frac{1}{4\pi} \int 2A'_{mk} n_k dS = -\frac{1}{2\pi} \int F_{mkp,p} n_k dS. \quad (5.12)$$

But such an expression is essentially the surface integral of a curl and therefore vanishes if the surface is closed (see Einstein and Infeld 1949, p. 213).

Therefore the result: no additional terms appear in the equations of motion. In this approximation, we can not obtain the equations of motion. Since this approximation is the only one that can give the terms in which the products $e e$ appear, that is, the products of charges, then the proper equations of motion cannot be obtained by the use of the new approximation method. This is the more surprising since the old-fashioned approach, in which the energy momentum tensor of the electromagnetic field is used, does give right equations of motion (see Infeld and Wallace 1940). One might think perhaps that an independent and purely geometric invariant formulation of the equations of motion can be given. That is, we might assume that the equations of motion are

$$\frac{d^2 \xi^m}{ds^2} + \sum_{a,b=0}^3 \Gamma_{ab}^m \frac{d\xi^a}{ds} \frac{d\xi^b}{ds} = 0; \quad m=0,1,2,3. \quad (5.13)$$

But this is not so. Indeed, if we develop (5.13) up to the second order we have

$$\ddot{\xi}^m + \left\{ \begin{matrix} m \\ 00 \end{matrix} \right\} = 0,$$

since $M_{00}^m = 0$. Thus again we obtain only the Newtonian equations of motion.

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LETTERS TO THE EDITOR

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On the Interaction of Particles in Feynman's Theory *)

by J. RZEWUSKI

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In a recent paper Feynman¹ developed a method for calculating Heisenberg's S-matrix as an expansion in powers of the coupling constant. The method consists in studying the dependence of the solutions of the Schrödinger equation on their boundary values. The interaction of particles is deduced by a generalization of the Coulomb potential.

In view of the importance of the problem of interaction and of the fact that Feynman's theory seems to give rise to ambiguities in the case of nucleons interacting by means of charged vector mesons, we wish to discuss a different method of introducing the interaction of particles in the frame work of the general theory of Feynman.

As an example to illustrate the method we consider the case of nucleons interacting by means of a charged vector meson field. Take the transition of two nucleons a and b from the states $\psi_a(1)$, $\psi_b(2)$ to the states $\varphi_a(3)$, $\varphi_b(4)$ under the influence of a mutual interaction which we assume to be small. (Feynman's notation is used throughout this letter). We may regard this process in the first approximation as a simple scattering of nucleon a in the field of b and of b in the field of a . To a transition of nucleon b from the state $\psi_b(2)$ to the state $\varphi_b(4)$ corresponds a certain current density $j_\mu^{(e)}(6)$. About this unknown current density one may make one obvious assumption: that it depends linearly on the state ψ as well as on φ . Thus

$$j_\mu^{(e)}(6) = g \int \int d^3x_1 d^3x_2 \varphi_b(4) \beta_b \cdot X_{\mu b}^{(e)}(6; 4, 2) \beta_b \psi_b(2), \quad (1)$$

where $X_{\mu b}^{(e)}(6; 4, 2)$ is an unknown matrix function of the points 2, 4 and 6. To find the action of particle b on a it is necessary to make some further assumptions as to the connection of field and current. As we wish to describe the interaction in terms of a charged vector meson field we assume the simplest covariant equation for a complex vector field having a positive definite energy. Such is the equation of Proca:

$$(\square - \kappa^2) A_\mu^{(e)} = -4\pi g \left(j_\mu^{(e)} + \frac{1}{\kappa^2} \frac{\partial}{\partial x_\mu} \cdot \frac{\partial j_\nu^{(e)}}{\partial x_\nu} \right). \quad (2)$$

* Reported at the Conference of Theoretical Physics, Toruń, May 1950. The full account of this work is in press in the Stud. Soc. Sc. Torunensis.

¹ Feynman R. P., Phys. Rev., **76**, 749 and 769 (1949).

The solution of this equation may be written

$$A_{\mu}^{(e)}(2) = -4\pi g \int F_{\mu\nu}(2, 1) j_{\nu}^{(e)}(1) d^4 x_1, \quad (3)$$

where the kernel $F_{\mu\nu}$ satisfies

$$(\square - \kappa^2) F_{\mu\nu}(2, 1) = \left(\delta_{\mu\nu} + \frac{1}{\kappa^2} \frac{\partial^2}{\partial x_{\mu 1} \partial x_{\nu 1}} \right) \delta(2, 1). \quad (4)$$

The Fourier integral representation of $F_{\mu\nu}$ is

$$F_{\mu\nu}(2, 1) = \frac{1}{(2\pi)^4} \int \frac{\delta_{\mu\nu} - \frac{1}{\kappa^2} k_{\mu} k_{\nu}}{k^2 - \kappa^2} e^{-ikx_2} d^4 k. \quad (5)$$

Assuming positive energy mesons moving forwards in time only, one gets the condition that the integration path must pass the negative pole in the integrand of (5) in the lower half of the complex k_4 -plane. The path around the positive pole is arbitrary and may be chosen in the upper half plane.

Now the first order amplitude for a transition of a from the state ψ_a to φ_a in the potential $A_{\mu}^{(e)}(5)$ is

$$-i \int \int d^3 x_3 d^3 x_3 \bar{\varphi}_a(3) \beta_a K_{+a}(3, 5) \underline{A}_{\tau}^{(e)} K_{+a}(5, 1) \beta_a \psi_a(1), \quad (6)$$

as follows from the Schrödinger equation for nucleons:

$$(i \underline{\nabla} - m - \sum_{\rho=1}^2 A_{\tau}^{(e)} \tau^{(\rho)}) \psi = 0. \quad (7)$$

The function K_{+} in (6) is the transition amplitude of Feynman:

$$K_{+}(2, 1) = \frac{i}{(2\pi)^4} \int \frac{e^{-ikx_2}}{k - m} d^4 k. \quad (6')$$

By (3) and (1) the amplitude (6) takes the form

$$\int \int \int d^3 x_1 d^3 x_2 d^3 x_3 d^4 x_4 \bar{\varphi}_a(3) \beta_a \bar{\varphi}_b(4) \beta_b \cdot K_{+}^{(1)}(3, 4; 1, 2) \cdot \beta_a \psi_a(1) \beta_b \psi_b(2). \quad (8)$$

with

$$\begin{aligned} & K_{+}^{(1)}(3, 4; 1, 2) \\ &= 4\pi i g^2 \sum_{\rho=1}^2 \int \int d^4 x_5 d^4 x_6 K_{+a}(3, 5) \gamma_{\mu a} \tau_a^{(\rho)} K_{+a}(5, 1) \cdot F_{\mu\nu}(5, 6) \cdot X_{\nu b}^{(\rho)}(6; 4, 2). \end{aligned} \quad (9)$$

The integrand in (9)

$$K_{+a}(3, 5) \gamma_{\mu a} \tau_a^{(\rho)} K_{+a}(5, 1) \cdot F_{\mu\nu}(5, 6) \cdot X_{\nu b}^{(\rho)}(6; 4, 2). \quad (10)$$

describes the action of b on a and must, of course, be equal to the action of a on b , which is, by similar arguments,

$$X_{\mu a}^{(\rho)}(5; 3, 1) \cdot F_{\mu\nu}(5, 6) \cdot K_{+b}(4, 6) \gamma_{\nu b} \tau_b^{(\rho)} K_{+b}(6, 2). \quad (11)$$

From the identity of (10) and (11) for all points 1, 2, 3, 4, 5, and 6 for all kinds of transitions it follows that

$$X_{\mu a}^{(e)}(5; 3, 1) = \text{const} \cdot K_{+a}(3, 5) \gamma_{\mu a} \tau_a^{(e)} K_{+a}(5, 1). \quad (12)$$

Putting $\text{const} = 1$ we obtain:

$$j_{\mu}^{(e)}(6) = g \int \int d^3 x_4 d^3 x_2 \bar{\varphi}(4) \beta K_{+}(4, 6) \gamma_{\mu} \tau^{(e)} K_{+}(6, 2) \beta \psi(2) = g \bar{\varphi}(6) \gamma_{\mu} \tau^{(e)} \psi(6) \quad (13)$$

and

$$K_{+}^{(1)}(3, 4; 1, 2) = 4\pi i g^2 \sum_{\varrho=1}^2 \int \int d^4 x_5 d^4 x_6 K_{+a}(3, 5) \gamma_{\mu a} \tau_a^{(e)} K_{+a}(5, 1) \cdot F_{\mu\nu}(5, 6) \cdot K_{+b}(4, 6) \gamma_{\nu b} \tau_b^{(e)} K_{+b}(6, 2). \quad (14)$$

This is the solution of the problem of interaction in the first approximation. The zero order approximation is, of course,

$$K_{+}(3, 4; 1, 2) = K_{+a}(3, 1) K_{+b}(4, 2). \quad (15)$$

Higher approximations may be written down immediately or deduced by similar methods.

For the case of no interaction, $\varphi = \psi$ and

$$j_{\mu}^{(3)} = g \bar{\psi} \gamma_{\mu} \tau^{(3)} \psi \quad (16)$$

becomes the usual Dirac current which justifies the assumption $\text{const} = 1$ in (12). In the case of interaction, the current (13) has the character of a fluctuation current. The total charge corresponding to (13) is zero in this case.

Statistical Interpretation of the Klein-Gordon Equation *)

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It is possible to find a statistical interpretation of the equations containing time derivatives of second and higher orders by a method similar to that used for the Schrödinger equation. This enables us to calculate cross sections for scattering processes involving waves obeying various types of fields equations without help of the quantum theory of fields. We shall explain the procedure on the special case of the Klein-Gordon equation with a given perturbation

$$(\square - m^2) \psi = g \varphi \psi, \quad (1)$$

where $\psi(x)$ is a complex field, $\varphi(x)$ a given external potential, g a small coupling constant and $x(x_{\mu})$ a point of the space-time. To distinguish points we shall often

* Part of lectures held at the Theoretical Physics Conference in Zakopane-Kuźnice, August 7—26, 1950.

write 1, 2, ... instead of x', x'', \dots . It is most convenient to use the Green-function treatment of field equations introduced by Feynman¹ (cf. also Rzewuski²). We first express the solution of (1) by means of the boundary values on a hypersurface consisting of two hyperplanes $t=t'_1$ and $t=t''_1$ and an arbitrary timelike hypersurface connecting those planes at infinity. The contribution from the latter vanishes and we get

$$\psi(2) = \int \psi(1') X_4(1') G(1'2) d^3 x'_1 - \int \psi(1'') X_4(1'') G(1''2) d^3 x''_1. \quad (2)$$

Here $t''_1 > t_2 > t'_1$, $d^3 x = dx dy dz$,

$$X_4(x) = \frac{\overrightarrow{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t} \quad (3), \quad G(12) = \sum_{n=0}^{\infty} G^{(n)}(12), \quad (4)$$

$$G^{(n)}(12) = g \int G^{(0)}(13) \varphi(3) G^{(n-1)}(32) d^4 x_3 \quad (5)$$

and

$$G^{(0)}(12) = \frac{1}{(2\pi)^4} \int \frac{e^{-ikx_{12}}}{k^2 - m^2} d^4 k, \quad kx_{12} = k_\mu(x_{1\mu} - x_{2\mu}). \quad (6)$$

The integrand in (6) has two poles at $k_4 = \pm \sqrt{\vec{k}^2 + m^2}$. To give (6) an unambiguous meaning we fix the path of integration so as to make it pass the negative pole on an infinitesimal circle in the lower half of the complex k_4 -plane and the positive pole in the upper half of this plane. The consequence of this prescription is that the operator $X_4(1)G^{(0)}(12)$ propagates plane waves

$$\psi^0(x) = \psi^0(p) e^{-ipx}, \quad p^2 = m^2 \quad (7)$$

with positive energy ($p_4 > 0$) forwards in time and the complex conjugate of (7) backwards in time:

$$\int \psi^0(1) X_4(1) G^{(0)}(12) d^3 x_1 = \begin{cases} \psi^0(2) & \text{for } t_2 > t_1 \\ 0 & \text{,, } t_2 < t_1 \end{cases} \quad (8)$$

$$\int \psi^{0*}(1) X_4(1) G^{(0)}(12) d^3 x_1 = \begin{cases} 0 & \text{,, } t_2 > t_1 \\ -\psi^0(2) & \text{,, } t_2 < t_1. \end{cases} \quad (9)$$

With help of (2), (4), (5), (8) and (9) we may express the solution of (1) by means of $G^{(0)}$, φ and the incoming plane wave $\psi_1^0(x)$

$$\psi_1(2) = \psi_1^0(2) + g \int G(23) \varphi(3) \psi_1^0(3) d^4 x_3, \quad (10)$$

and similarly the solution of the complex conjugate equation to (1) if ψ_2^0 denotes the outgoing plane wave

$$\psi_2^*(2) = \psi_2^{0*}(2) + g \int d^4 x_3 \psi_2^{0*}(3) \varphi(3) G(32), \quad (11)$$

the only assumption being $t'_1 \rightarrow -\infty$, $t''_1 \rightarrow +\infty$.

¹ Feynman R. P., Phys. Rev., **76**, 749 (1949).

² Rzewuski J., Stud. Soc. Sc. Torunensis (in press); Acta Phys. Polonica, preceding letter.

Now we ask for the probability amplitude for scattering in the external field φ of the plane wave ψ_1^0 at $t_1' = -\infty$ into the state ψ_2^0 at $t_1'' = +\infty$. In the case of the Schrödinger equation we argue as follows: At $t_1' = -\infty$ we have an incoming plane wave ψ_1^0 which is the solution of the unperturbed Klein-Gordon equation. The perturbation φ changes ψ_1^0 into say ψ_1 which is the solution of the full equation. On a hypersurface say $t = t_1''$ this ψ_1 may be considered as a superposition of plane waves like (7). The probability amplitude that at a measurement we find the state ψ_2^0 is simply the corresponding expansion coefficient

$$\int \psi_2^{0*}(1'') \psi_1(1'') d^3x_1'' \quad (12)$$

if the ψ^0 are normalized to unity. This coefficient is independent of the time t_1 in the limit $t_1 \rightarrow +\infty$.

We generalize this procedure for the Klein-Gordon equation and take

$$A(\psi_1^0 \rightarrow \psi_2^0) = \int \psi_2^{0*}(1'') Y(1'') \psi_1(1'') d^3x_1'' \quad (13)$$

as the transition amplitude $\psi_1^0 \rightarrow \psi_2^0$. Here $\psi_1(1'')$ depends linearly on the initial state $\psi_1^0(1')$ according to (10) and $Y(1'')$ is an unknown operator. The linear dependence on the initial and final state is necessary in view of the linearity of quantum theory. The operator $Y(x)$ is easily determined by a symmetry argument. Indeed, by means of (11), we can express $\psi_2^*(1')$ by the outgoing wave $\psi_2^{0*}(1'')$ at $+\infty$. Thus the same transition amplitude may be written

$$A(\psi_1^0 \rightarrow \psi_2^0) = \int \psi_2^{0*}(1') Y'(1') \psi_1^0(1') d^3x_1', \quad (14)$$

where Y' is another unknown operator. It is understood that in (13) the limit $t_1'' \rightarrow \infty$ and in (14) $t_1' \rightarrow -\infty$ is taken. From the identity of (13) and (14) for all possible ψ_1^0 and ψ_2^0 it follows that

$$Y(x) = Y'(x) = X_4(x) = \frac{\partial}{\partial t} - \frac{\partial}{\partial t}. \quad (15)$$

Normalizing the plane waves in such a way that the unperturbed transition $\psi_1^0 \rightarrow \psi_1^0$ has an amplitude of modulus one, we get

$$\psi_1^0(p) = \frac{1}{\sqrt{2p_4V}}, \quad (16)$$

where V is the considered volume of space. Now we can finally write (13) or (14) in either of the forms

$$\begin{aligned} A(\psi_1^0 \rightarrow \psi_2^0) &= -i \delta_{\psi_1^0 \psi_2^0} - g \int d^4x \psi_2^{0*}(x) \varphi(x) \psi_1(x) = \\ &= -i \delta_{\psi_1^0 \psi_2^0} - g \int d^4x \psi_2^*(x) \varphi(x) \psi_1^0(x). \end{aligned} \quad (17)$$

Here $\delta_{\psi_1^0 \psi_2^0} = \begin{cases} 1 & \text{if } p_1 = p_2 \\ 0 & \text{if } p_1 \neq p_2 \end{cases}$. (We consider a finite V and therefore a discrete spectrum of the p 's. In the case of continuous spectrum the δ -function should be used). We

may note that the final result (17) has not the covariant form of (10) or (11). This is caused by the non-invariance of the definition of the transition amplitude and the resulting non-invariance of the normalization procedure. However, the physically important second terms of both forms of (17) become relativistically invariant after multiplication with $\sqrt{(p_1)_4(p_2)_4}$, e. g.

$$-g \sqrt{(p_2)_4} \int d^4x \psi_2^{0*}(x) \varphi(x) \psi_1(x) \cdot \sqrt{(p_1)_4}. \quad (18)$$

An analogous procedure may be applied to relativistic equations of higher order. A full account of this work will be published shortly in this journal.

Coincidences in GM-Counters due to Single Gamma-Photons

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Mięsowicz, Jurkiewicz and Massalski^{1,2} showed that in the measurements of cosmic radiation at great depths the excess of twofold over threefold coincidences in a counter telescope can be explained by local γ -radiation. They suggested the following mechanism of these coincidences: the γ -quantum going through the first counter discharges it by producing a Compton-electron and the scattered photon discharges the second counter. The possibility of such coincidences was mentioned already by Dunworth³. These coincidences may be easily observed in scintillation counters, as was shown by Hofstadter and McIntyre⁴. Beringer⁵ observed their very small influence on the results of measurements of angular correlation of γ -rays emitted in cascade.

The aim of the present experiments has been to investigate the mechanism of such coincidences in GM-counters. A collimated beam of ThC'' γ -rays filtered through 25 mm of lead has been directed to a first counter and scattered in it. The scattered γ -radiation has been registered in a second counter working in coincidence with the first one. This counter telescope could be rotated around the axis of the first counter. The rate of coincidences at different angles between the γ -ray beam and the axis of the telescope has been registered by means of a coincidence circuit with a resolving time of 0,36 μ sec. The curve in Fig. 1 shows a distinct maximum of the rate of coincidences at about 28°. Assuming that the coincidences are caused by Compton scattering of the γ -rays in the first counter, I have calculated the theoretical curve of the angular distribution of the coincidences, based on the formula of Klein and Nishina, the known ranges of the Compton electrons in the material of the wall of the counter and the dependence of the efficiency of the counter on the

¹ Mięsowicz M., Jurkiewicz L. and Massalski J. M., Phys. Rev., **77**, 380 (1950); Acta Phys. Polonica, **10**, 69 (1950).

² Mięsowicz M. and Massalski J. M., Acta Phys. Polonica, **11**, 274 (1951).

³ Dunworth J. V., Rev. Sci. Instrum., **11**, 167 (1940).

⁴ Hofstadter R. and McIntyre J. A., Phys. Rev., **76**, 1296 (1949).

⁵ Beringer R., Phys. Rev., **63**, 23 (1943).

energy of γ -radiation. The curve which I have got agrees very well with the data of the measurements, as can be seen from Fig. 1.

Using these data it is also possible to estimate the rate of coincidences in the double telescope working in a space filled with isotropic γ -radiation. The rate of the

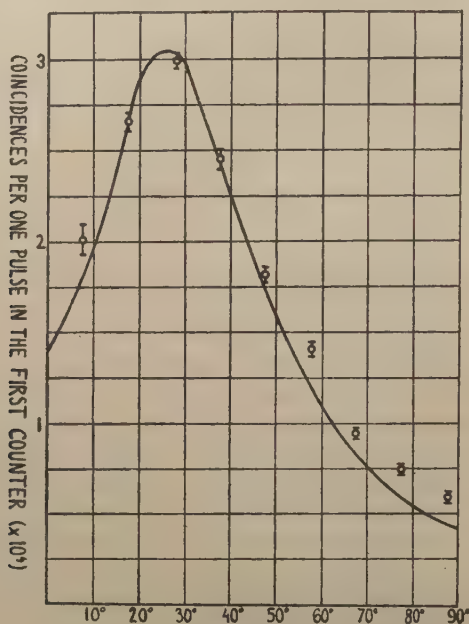


Fig. 1

coincidences estimated in this way is of the same order as found by Mięsowicz and Massalski² in their measurements in a salt mine. A more detailed account will be published shortly in this journal.

I express my indebtedness to Professor M. Mięsowicz for suggesting the subject of the research and for the kind interest and many valuable discussions during its course.

Non-Local Quantum Electrodynamics

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January 18, 1950

A non-local electrodynamics based on the reciprocal commutation relations of Yukawa¹ is investigated. The non-local spinor field in vacuo obeys the following commutation relations

$$\{\psi_{\alpha}(x, r), \bar{\psi}_{\beta}(x', r')\} = \frac{1}{i} S_{\alpha\beta}(x - x', r, r'), \quad (1)$$

¹ Yukawa H., Phys. Rev., **77**, 219 (1950). See also Born M., Proc. Roy. Soc. Edinb., **A 62**, 40 (1944).

where generalized $S(x, r, s)$ function may be defined (together with other S -like functions) in the following way: Let \hat{S} denote any one of the well known $S, \bar{S}, S^{(1)}$ etc. ... functions, then

$$\bar{S}(x, r, s) = \left(\gamma^\mu \frac{\partial}{\partial x_\mu} - m \right) \hat{\Delta}(x, r, s), \quad (2)$$

where the Fourier transform of the $\hat{\Delta}$ function is

$$\hat{\Delta}(k, r, s) = \hat{\Delta}(k) \varrho(k, r) \varrho(k, s), \quad (3)$$

where $\hat{\Delta}(k)$ is the Fourier transform of the usual $\hat{\Delta}(x)$ function, well known from the electrodynamics of Schwinger, while

$$\varrho(k, r) = \frac{\delta(k_\mu r_\mu) \delta(r_\mu r_\mu + \lambda^4 k_\mu k_\mu)}{\int d^4 r \delta(k_\mu r_\mu) \delta(r_\mu r_\mu + \lambda^4 k_\mu k_\mu)}. \quad (4)$$

The field quantities obeying the Dirac equation and the commutation relation (1) are

$$\psi(x, r) = \sum \psi_n(x) \varrho(k^{(n)}, r), \quad (5)$$

where $\psi_n(x)$ are plane waves with the wave vector $k_\mu^{(n)}$ well known from the usual theory of fermions.

A general correspondence rule²

$$a(x) = \int d^4 r a(x, r) \quad (6)$$

enables to construct the densities of observables with the aid of the matrix multiplication law. For the current density we get

$$j_\mu(x) = \int d^4 r d^4 s s_\mu(y, r, s) \quad (7)$$

with

$$s_\mu(y, r, s) = \frac{1}{2} [\bar{\psi}(y, s), \gamma^\mu \psi(y, r)], \quad (8)$$

where

$$y = x - \frac{1}{2}(r + s). \quad (9)$$

The most natural form of field equations with a non-localized interaction is constituted by integral equations avoiding the infinitesimal point of view. We express, therefore, the interaction with the electromagnetic field by means of some integral equations written in terms of advanced and retarded potentials

$$A_\mu(x) = A_\mu^{in}(x) + \int d^4 x' D^{ret}(x - x') j_\mu(x') \quad (10)$$

$$\psi(y, r) = \psi^{in}(y, r) - \frac{ie}{2} \int dP' S^{ret}(y - y', r, s') \{ \gamma^\mu \psi(y', r'), A_\mu(x') \}, \quad (11)$$

where

$$dP' = d^4 x' d^4 r' d^4 s' = d^4 y' d^4 r' d^4 s'. \quad (12)$$

² Rayski J., Acta Phys. Polonica, **10**, 103 (1950).

Similar equations hold for the advanced potentials. The above equations are invariant under the restricted group of linear gauge transformations

$$A_\mu(x) \rightarrow A_\mu(x) - \frac{\partial f(x)}{\partial x_\mu}, \quad \psi(y, r) \rightarrow \psi(y, r) e^{-ie f(y)}, \quad (13)$$

where f is a linear function

$$f(x) = a_\mu x_\mu + b. \quad (13')$$

The linear gauge invariance is sufficient to make constant potentials meaningless and seems physically acceptable.

The general method of quantization consists on assuming for the ingoing (and outgoing) waves the commutation relations for the fields in vacuo (without interaction). The commutation relations for the perturbed waves then follow automatically from the integral field equations. This method of quantization avoids the canonical formalism and is applicable to a wide class of field equations with a non-localized interaction. The S -matrix may be constructed by means of a procedure due to C. N. Yang³. In our case we have

$$A_\mu(x) = A_\mu^{(0)}(x) + \frac{ie}{2} \int dP' \bar{D}(x-x') [\bar{\psi}(y', s'), \gamma^\mu \psi(y', r')], \quad (14)$$

$$\psi(y, r) = \psi^{(0)}(y, r) + \frac{e}{2i} \int dP' \bar{S}(y-y', r, s') \{\gamma^\lambda \psi(y', r'), A_\lambda(x')\}, \quad (15)$$

$$[A_\mu^{(0)}(x), S] = \frac{-ie}{4} \int dP' D(x-x') \{S, [\bar{\psi}(y', s'), \gamma^\mu \psi(y', r')]\}, \quad (16)$$

$$[\psi^{(0)}(y, r), S] = \frac{-e}{4i} \int dP' S(y-y', r, s') \{S, \{\gamma^\lambda \psi(y', r') A_\lambda(x')\}\}, \quad (17)$$

where the quantities labelled with the index zero mean half the sum of advanced and retarded potentials, while S is the S -matrix of Heisenberg. (14) may be substituted into (15), (16) and (17) so that we obtain new equations dependent upon $A_\mu^{(0)}$ only (and not upon A_μ). Then, (14) may be treated as a definition of A_μ and not as one of the equations. Thus, we are released from the necessity of investigating the auxiliary condition for the perturbed A_μ but may limit ourselves to $A_\mu^{(0)}$ only. The Lorentz condition is simply

$$\frac{\partial A_\mu^{(0)}}{\partial x_\mu} \Big|_{>0} = 0, \quad (18)$$

which reduces to two well known initial conditions.

There is little doubt in the compatibility of (15), (16) and (17) together with the (interaction free) commutation relations for $A_\mu^{(0)}$ and $\psi^{(0)}(y, r)$ and in the existence of an S -matrix. The S -matrix elements obtained from (14), (15), (16) and (17) differ from the traditional ones by the fact that every $\psi(x)$, $\bar{\psi}(x)$, $\tilde{S}(x'-x'')$ is replaced by its non-local counterpart taken at the translated point y : $\psi(y, r)$, $\bar{\psi}(y, s)$, $\tilde{S}(y'-y'', r', s')$, while the integrations $\int d^4x' d^4x'' \dots$ are supplemented to threefold integrations $\int dP' dP'' \dots$. This is a general rule for an immediate transcription of the usual S -matrix into the non-local form. The new S -matrix differs from the usual one by a set of relativistic convergence factors. The usual convergence difficulties are expected to be surmounted by the above non-local formalism.

³ Yang C. N., forthcoming paper in Phys. Rev. See also Källén, Arkiv för Fysik, **2**, 371 (1950).

Relativistically Invariant Homogeneous Canonical Formalism With Higher Derivatives

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Just over one hundred years ago Ostrogradzky (1850) showed how to apply Hamilton's canonical formalism to problems in the Calculus of Variation involving second (or higher) derivatives as arguments in the function under the sign of integration. Recently attention has been drawn to the fact (cf., e. g., Bopp 1948) that the introduction of second derivatives in the Lagrangian function may lead to promising results in connection with the dynamics of elementary particles and its quantization. On the other hand it is well known that to treat all the four space-time variables on the same footing, it is necessary to consider the time as a fourth canonical coordinate and introduce an auxiliary parameter (without physical significance) acting as integration variable in the expression for the action in the „homogeneous Hamilton principle“ and as differentiation variable in the corresponding Euler-Lagrange equations.

The Hamilton-Ostrogradzky principle has been put therefore in „parametric“ or „homogeneous“ form by writing it as

$$\delta \int_{\pi_1}^{\pi_2} d\pi \mathcal{L}(x^\mu, x'^\mu, x''^\mu) = 0, \quad (1)$$

where primes denote differentiation with respect to the arbitrary parameter π , the variation of the independent variable π vanishes identically and the variations of the dependent variables $x^\mu = x^\mu(\pi)$ vanish at the ends of the path of integration; $\mu = 1 \dots 4$ (or, more generally, $1 \dots n$). For the integral in (1) not to depend on the choice of the parameter π , \mathcal{L} must satisfy the two following identities

$$\mathcal{L} = x'^\mu \frac{\partial \mathcal{L}}{\partial x'^\mu} + 2x''^\mu \frac{\partial \mathcal{L}}{\partial x''^\mu}, \quad (I)$$

$$x'^\mu \frac{\partial \mathcal{L}}{\partial x''^\mu} = 0, \quad (II)$$

the first expressing the independence of the integral in (1) with respect to linear changes of parametrization, the second — with respect to other, non-linear, changes. As is well known, the corresponding Euler-Lagrange equations are

$$\frac{\partial \mathcal{L}}{\partial x^\mu} \equiv \frac{\partial \mathcal{L}}{\partial x^\mu} - \frac{d}{d\pi} \left(\frac{\partial \mathcal{L}}{\partial x'^\mu} - \frac{d}{d\pi} \frac{\partial \mathcal{L}}{\partial x''^\mu} \right) \quad (2)$$

Call $x'^\mu = w^\mu$, introduce

$$n_\mu = \frac{\partial \mathcal{L}}{\partial w^\mu} \quad (3)$$

and put

$$p_\mu = \frac{\partial \mathcal{L}}{\partial w^\mu} - \dot{n}_\mu. \quad (4)$$

In (3), (4), and from now on, \mathcal{L} has to be considered as a function of x^μ , w^μ and \dot{w}^μ . Identity (II) becomes

$$n_\mu w^\mu = 0 \quad (\text{II a})$$

and both identities (I) and (II) yield

$$\mathcal{L} = p_\mu w^\mu + n_\mu w^\mu. \quad (\text{III})$$

Because of (IIa) equations (3) cannot be solved for \dot{w}^μ ; we assume that there are no further relations between x^μ , w^μ and n_μ — except (II a). There must exist, however, a relation between x^μ , w^μ , n_μ and p_μ , which we may obtain by eliminating w^μ from (3) and (III). Let us write this relation in the form

$$\mathcal{H}(x^\mu, p_\mu; w^\mu, n_\mu) = 0. \quad (5)$$

We assume also that there are no other relations between x^μ , p_μ , w^μ and n_μ but, obviously, the relation (5) may be put in other, equivalent, forms. There exist thus in this case — as is well-known from the similar case of the parametric form of Hamilton's principle without higher derivatives — an infinity of Hamilton's functions.

The canonical equations may then be written, as follows

$$\begin{aligned} \dot{x}^\mu &= \lambda \frac{\partial \mathcal{H}}{\partial p_\mu}, & \dot{p}_\mu &= -\lambda \frac{\partial \mathcal{H}}{\partial x^\mu}; \\ \dot{w}^\mu &= \lambda \frac{\partial \mathcal{H}}{\partial n_\mu} + \lambda_1 \dot{w}^\mu, & \dot{n}_\mu &= -\lambda \frac{\partial \mathcal{H}}{\partial w^\mu} - \lambda_1 n_\mu. \end{aligned} \quad (6)$$

It can be further shown that the Lagrangian function of a spin-particle, or rather its part depending on the four-dimensional „quasi-acceleration“ \dot{w}^μ is proportional to the fourth root of the square of the modulus of the „transverse quasi-acceleration“ $\dot{w}^\mu - \frac{w_\lambda \dot{w}^\lambda}{w_\nu w^\nu} w^\mu$ (eq. (7) below), this being a consequence of the following three assumptions: (1) it is Lorentz invariant, (2) it does not depend on the arbitrary choice of the parametrization, and (3) it neither vanishes nor becomes infinite when $w_\mu w^\mu$ tends to zero, i. e., when the velocity of the (three-dimensional) singularity¹ tends to the velocity of light.

To ensure continuity with relativistic dynamics of particles without spin, we must add the usual Lagrangian function for this case. Thus, we can finally write the expression for the Lagrangian function of a spin particle with any velocity not exceeding the velocity of light, as follows

$$\mathcal{L} = -2\gamma \left[\sqrt{-w_\mu w^\mu} + \sqrt{l} \sqrt{\dot{w}_\mu \dot{w}^\mu - \frac{(w_\lambda \dot{w}^\lambda)^2}{w_\nu w^\nu}} \right]. \quad (7)$$

As \mathcal{L} is only defined to an arbitrary factor γ is a constant without physical significance, from the point of view of the present variational principle, l is a universal constant with the dimensions of length.

¹ From the point-of-view exposed in 1948 (Weyssenhoff 1948 a) not the singularity itself but rather its mean position has to be considered as the relativistic model of an elementary particle with non-vanishing spin.

As a first application of our variational principle the equations of motion of: (a) a spin-particle moving with a velocity smaller than that of light (Frenkel 1926, Mathisson 1937), (b) a „pole-dipole particle“ (Hönl and Papapetrou 1940), and (c) a spin-particle moving with the velocity of light (Weyssenhoff and Raabe 1948) may be deduced as particular cases and their interdependence elucidated.

Perhaps it is also worth mentioning that, due to the appearance of the fourth root in the expression for the Lagrangian function, the theory cannot be considered as a whole without the use of complex numbers.

The full text will appear in the next issue of this Journal.

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